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Donor-acceptor interactions in polycondensation processes

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ABSTRACT. **The results of studies on the role of donor-acceptor interactions in polycondensation processes are correlated. The thermodynamic and kinetic aspects of the problem, the features of the reaction mechanism, structure and properties of the resulting polymer that are related to donor-acceptor interactions are examined in examples of the curing of epoxide oligomers.**

The bibliography includes 84 references.

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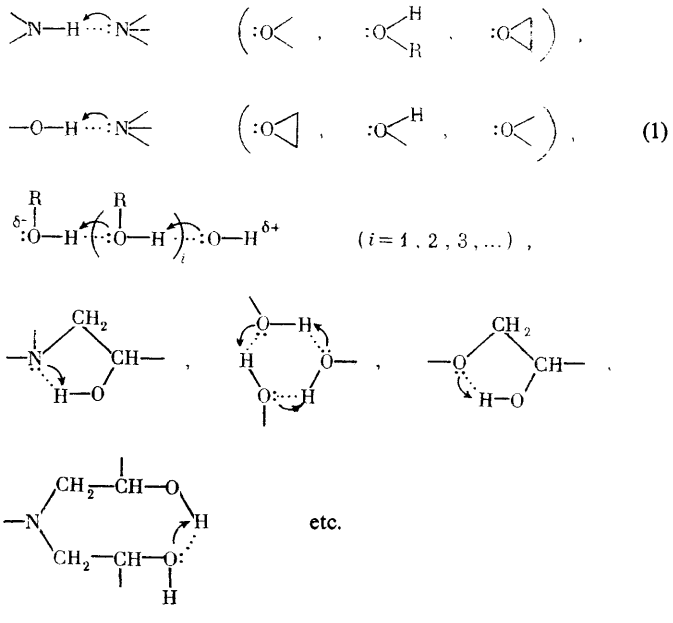
I. Introduction

Monomers containing reactive functional groups of an electrophilic and nucleophilic nature are usually employed as starting compounds in polycondensation processes. These groups can undergo different donor-acceptor interactions between themselves and with other compounds of the reaction system (polymer, solvent, catalyst, impurities or specially introduced components), forming homo- or hetero-associates of a linear or cyclic nature. Thus, both initial and developing systems have a well-defined structural organisation. Although the very fact of such donor-acceptor interactions occurring between polar groups has been known for a long time in organic chemstry, their role in polycondensation processes during the formation of linear and cross-linked polymers, as in similar reactions of low-molecular-weight organic compounds, has until recently remained unclear. Only comparatively recently has this question become the subject of systematic studies, mainly through the efforts of two groups of research workers at the Semenov Institute of Chemical Physics, USSR Academy of Sciences. The first group has studied this question in the case of reactions involving formation of urethanes,[1–12] the second group has studied epoxide curing processes.[13–31] On the basis of these studies it has been possible to formulate sufficiently well-argued ideas about the role of donor-acceptor interactions in the kinetics and mechanism of the processes studied and also in the formation of the structure and properties of the resulting polymers.

The aim of the present article is to classify the results of studies on the effect of donor-acceptor interactions on polycondensation processes, mainly by considering examples of the curing of epoxide oligomers and to draw the attention of research workers to this problem. Elucidation of the role of possible donor-acceptor interactions in the reaction system is a key not only to a more fundamental understanding of the features of the kinetics and mechanism of the formation of a polymer but also to controlling the process and, in individual cases, the structure and properties of the resulting polymer.

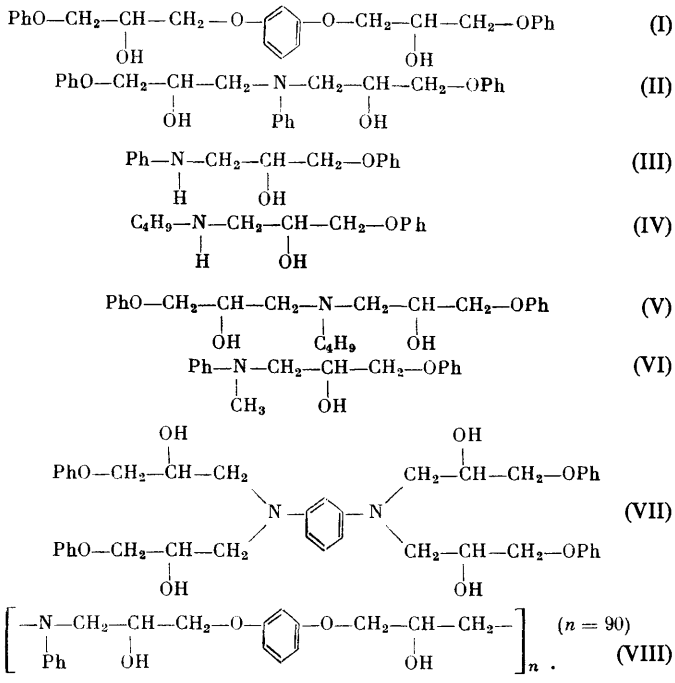
II. Composition of the reaction system

The composition of the reaction system is highly complex because of the occurrence of various donor-acceptor interactions, and linear and cyclic homo- and hetero-associates are contained in the system together with the monomer forms of reactive functional groups. As an example we can illustrate the possible forms of the donor-acceptor complexes for epoxyamine systems containing primary, secondary, and tertiary amino groups as well as epoxide, secondary hydroxyl, and ether groups.



The occurrence of such donor-acceptor interactions as described above was demonstrated using specially synthesised and certain other model compounds by means of IR spectroscopic studies over a

wide concentration range in CCl_4 solution.[13,20,26,27] The model compounds that were synthesised are depicted below:



The values of thermodynamic parameters for the respective complexation reactions have been determined by means of calorimetry and IR spectroscopy (Tables 1 and 2).[13,20,26,31–33]

Table 1. Thermodynamic parameters of reactions for the formation of model donor-acceptor complexes.[20]

Reaction system	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}	K_e*, litre mol^{-1}	K_e**, litre mol^{-1}
Cyclohexanol–cyclohexanol (HH)	27.2	98.6	–	–
Cyclohexanol–phenyl glycidyl ether (EH)	14.2	46.0	1.3/0.5	1.5/0.6
Cyclohexanol–aniline (A_1H)	18.8	67.0	1.9/0.5	2.0/0.5
Cyclohexanol–ethylaniline (A_2H)	11.7	41.8	1.4/0.7	1.2/0.6
Cyclohexanol–diethylaniline (A_3H)	3.8	8.4	0.6/0.6	0.3/0.3

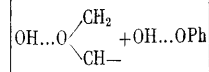
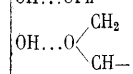
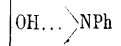
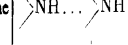
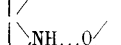
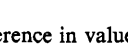
* The equilibrium constants K_e (determined by calorimetry) at 22 °C are given by the numerator, while the values of K_e at 98 °C are given by the denominator.

** The values of K_e (determined by IR spectroscopy) at 28 °C are given by the numerator, while the values of K_e at 98 °C are given by the denominator.

Five-membered rings constitute a characteristic form of the cyclic associates. In the molecules of model compounds II and V eight-membered rings with OH...OH hydrogen bonds also occur, but the total proportion of cyclic structures of the associates in the polymer is small and does not exceed 1–2%. A similar conclusion was also drawn from kinetic studies.[20,30]

It is interesting to note that NH groups participate in the formation of hydrogen bonds in both the crystalline and amorphous states of the compound not only as electron donors but also as acceptors.[26,32,33]

Table 2. Thermodynamic parameters of model H-complexes.[26,32,33]

Compound	Reaction system	Type of H-bond in the complex	K_e (at 25 °C), litre mol^{-1}	$-\Delta H$, kJ mol^{-1}
I	Isopropanol–isopropanol	OH...OH	2.45	17.0÷21.0
II	Isopropanol–phenyl glycidyl ether		1.08	–
III	Isopropanol–anisole	OH...OPh	0.33	9.6
IV	From the difference between systems II and III*		0.75	12.5
V	Isopropanol–*N*-diethylaniline		0.38	9.2
VI	*N*-Methylaniline–*N*-methylaniline		0.45	7.5
VII	*N*-Methylaniline–anisole		0.36	7.5
VIII	*N*-Methylaniline–di-n-propyl ether		0.29	13.0

* K_e calculated from the difference in values for systems II and III.

It can be seen from Table 2 that autoassociation of the hydroxyl groups is the predominant form of association at room temperature. As estimates have shown,[26] the proportion of hydroxyl group autoassociates in epoxyamine networks with a stoichiometric composition constitutes 85–90%. Autoassociation of hydroxyl-containing compounds (alcohols, phenols, acids) has been well studied. The extensive literature data, which have been classified in three reviews,[31,33,34] indicate that it is quite a complex process, resulting in the formation of an equilibrium mixture of different linear and cyclic *n*-dimensional autoassociates. With respect to the question that interests us concerning the participation of such structures in the catalysis of the nucleophilic addition of amines to an epoxide ring, the cyclic associates usually exist as trimers and it follows from their structure [see scheme (1)] that they are actually inactive in this process, whereas in linear associates the activity increases significantly relative to the activity of a monomeric hydroxyl-containing compound.

The question as to how information about the thermodynamics of low-molecular-weight model compounds can be applied to real cross-linked epoxyamine polymers is quite natural. A direct comparison between the IR spectra of model compounds and polymers provides a clear answer.[28] The frequencies of the absorption maxima, the line

half-widths, and the relative intensities of vibration bands due to groups participating in the formation of hydrogen bonds for model compounds (melt or glass) virtually match those of linear and cross-linked polymers in a vitreous state. This means that the composition and average values of the hydrogen bond energies for polymer and low-molecular-weight epoxyamine systems are similar. A similar conclusion can be made by comparing the thermodynamic parameters of the model and polymer systems (Tables 1–3).

Table 3. Thermodynamic parameters of complexation reactions for a number of epoxyamine systems.[13,17,18,23,24]

System	$-\Delta H$, kJ mol^{-1}	$-\Delta S$, J mol^{-1} K^{-1}
Phenyl glycidyl ether–aniline (Refs.20, 23)		
EH	9.6	29.3
A_1H	14.2	35.5
A_2H	9.2	27.2
Phenyl glycidyl ether–*N*-ethylaniline (Ref.24)		
EH	10.4	33.4
A_2H	10.4	41.8
A_3H	4.6	5.0
Resorcinol diglycidyl ether–2,5-diaminopyridine (Refs.17, 18, 21)		
EH	16.3	33.4
A_1H	14.2	31.3
A_2H	10.4	41.8
A_3H	4.6	5.0

The processes involving formation of donor-acceptor complexes in oligooxypropylene glycols, hydroxyoligobutadienes, and oligourethanes have been studied using IR spectroscopy and calorimetry.[34–36] It was shown that the thermal parameters of the H-complex in these systems (HO:...H–O, OH...:O<, OH...π-bond, NH...π-bond, NH...:O=C<) do not depend on the molecular weight of the oligomers and almost match those for low-molecular-weight model compounds.

All these results suggest that the approach using model systems to study donor-acceptor interactions is fully justified. Moreover, only with its application is it possible to determine quantitatively the thermodynamic and kinetic properties of the numerous complexes that are formed in a reaction system. At the present time we have only just begun to study the thermodynamics and kinetics of complex systems. For the time being, in fact, it is only possible to determine the apparent values of the thermodynamic and kinetic parameters in the systems (see Section III). The development of an algorithm for both experimental and theoretical approaches to the study of such systems remains an important task.

In studying the thermodynamics of these reactions another problem arises—a correct determination of the exothermicity of opening the epoxide ring and the justification for using calorimetry to study the kinetics of the process.

In fact, during the complexation reactions in the system with constantly varying concentrations of donor and acceptors, the apparent quantity of heat liberated (Q) may have a non-linear dependence on the degree of conversion (α) since in general

$$Q = q\alpha + \sum q_i(\alpha), \qquad (2)$$

where q is the exothermicity of opening the epoxide ring: $\Sigma q_i(\alpha)$ is the total exothermicity of all the donor-acceptor interactions in the system, which depends non-linearly on the degree of conversion $\alpha = (E_0 - E)/E_0$ (E and E_0 are the current and initial epoxide concentrations respectively).

However, it usually transpires that there is a well-defined linear relationship between Q and α, determined chemically or by means of IR spectroscopy (it is represented graphically as a straight line starting from the origin). Consequently, $\Sigma q_i(\alpha) \to 0$ and $q\alpha \gg \Sigma q_i(\alpha)$, namely, there is a balancing out of the heats of formation and heats of decomposition of the different complexes in the systems during the process. This in turn means that calorimetry can be used as a tool to study the kinetics of these reactions.

III. Donor-acceptor interactions and reaction kinetics

It is clear that formation of the complexes described above must lead to a change in the reactivity of the initial reactant molecules. At the same time, because the concentrations of the functional groups and hence donor-acceptor complexes are constantly changing throughout polycondensation, the nature of the kinetic effects must also vary with the conversion.

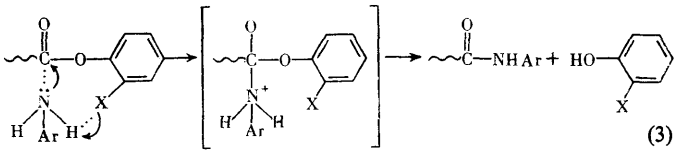
Only on the basis of ideas about the decisive role of complexation processes is it possible to understand such characteristics of the reactions of epoxy compounds with primary and secondary amines as the simultaneous occurrence of autoacceleration and autoinhibition effects, which is very unusual in terms of kinetics,[13,20,30] the catalytic and inhibitor effect of different solvents,[13,20,27–40] the well-defined ortho effect of electron-donating substitutents in aromatic amines and the anomalously low activity of polyoxyethylene primary amines,[37,41] the accelerating effect of added quantities of tertiary amines,[19,42] the high reactivity of aromatic *N*-diglycidylamines and *o*-diglycidyl ethers,[43,44] and certain others.[20,29,45–49]

A very typical kinetic feature of polycondensation systems that is related to the occurrence of donor-acceptor interactions is the markedly non-linear, and sometimes even non-monotonic, dependence of the rate of reaction on the concentration of the reactants with a considerable variation of the latter.[3–6,46,48]

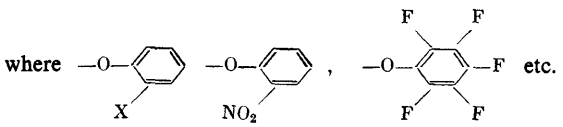
In the formation of urethanes during reaction between isocyanates and alcohols catalysed by tetravalent tin compounds, the effect of donor-acceptor interactions manifests itself in the extremal nature of the dependence of the catalytic rate constant on the strength of the complex between catalyst and alcohols,[50] the sharp reduction in the Hammett ρ constant compared to that for a non-catalytic process,[51] and the levelling out of the reactivity of hydroxyl groups that are different in nature.[3,4]

In reactions of the so-called "activated" polycondensation the high activity of *o*-substituted phenyl esters is due not only to and even not so much to stabilisation of the leaving group, which increases with a decrease in pK_a of the corresponding acid, but mainly to the catalytic effect of the *o*-substituent through formation

of an intramolecular hydrogen bond with amines in the preparation of a polyamide:[52,53]

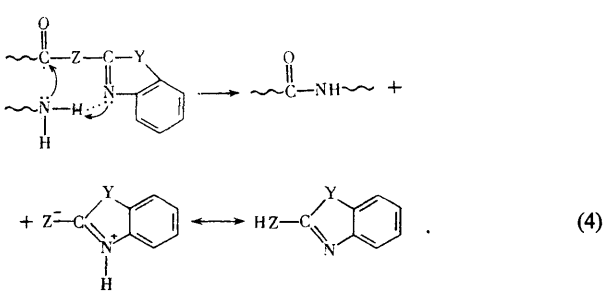


(3)

where  etc.

As expected, the catalytic effect of an *o*-substituent (such as NO_2) is particularly well defined in a proton-inert or weakly proton-accepting medium (chlorobenzene, benzene), where the *o*-nitrophenyl ester is two to four times more active than its *p*-substituted analogue. In a strong proton-donating medium (HMPA), which inhibits the formation of an intramolecular hydrogen bond, the reverse occurs—the *p*-nitrophenyl ester is eight times more active than the *o*-substituted isomer.[53]

It was established in a similar manner that benzene derivatives are very effective as leaving groups because of the formation of an intramolecular hydrogen bond in the reaction between activated esters and amines:[54]

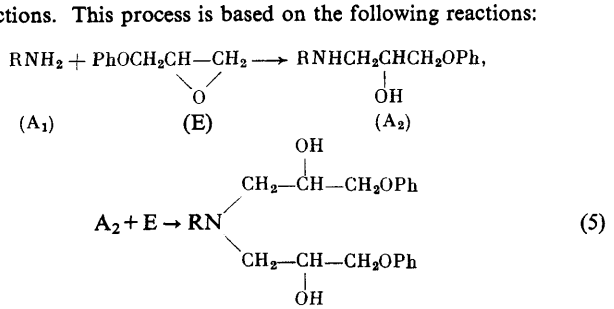


(4)

(Y, Z = —O—, —S—)

In a recently published monograph[55] a large number of examples are given to illustrate the determining role of an intramolecular hydrogen bond and other types of donor-acceptor interactions of reacting groups in the catalysis of different nucleophilic substitution-addition reactions.

Let us examine in greater detail the features of the kinetics of the curing of epoxides by amines that are related to donor-acceptor interactions. This process is based on the following reactions:

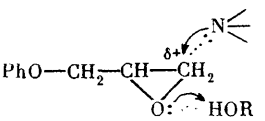


(5)

(R = Ar or Alk).

A tertiary amino group that is formed during curing of epoxides by aliphatic amines can in individual cases catalyse the polymerisation of epoxide groups. If aromatic amines are used as curing agents, this reaction does not occur at temperatures below ~150 °C.

It is widely known that added quantities of hydroxyl-containing compounds (water, alcohols, phenols, acids) substantially accelerate the reaction between epoxides and amines and other nucleophilic reactants.[18–24,56–63] In this case considerable activation of the carbon atom of the epoxide ring towards nucleophilic attack takes place. The reaction occurs via a trimolecular transition state, first described by Smith[62,63] for the interaction between epoxide compounds and amines: †



(6)

It is as a result of the build-up of hydroxyl groups during the reaction [see scheme (5)] that the curing of epoxide oligomers by amines has a well-defined autocatalytic nature.

By using a special method for the efficient removal of traces of moisture and other hydroxyl-containing compounds[22] from the initial materials and reaction vessels, it was possible to reduce the concentration of hydroxyl-containing impurities on the basis of water to 10^{-6} mol litre^{-1} or less.

It transpired[22] that under these conditions a reaction occurs between phenyl glycidyl ether (PGE) and aniline, but the initial rate is 40–50 times slower than in the reaction catalysed by proton donors and the dependence on the aniline concentration is quadratic rather than linear. The presence of even small amounts of moisture reduces the order of reaction with respect to amine.

The quadratic dependence of the rate of reaction on the concentration of amine (A_1) signifies that the latter acts both as an electrophile, forming an intermediate complex (A_1E) with an epoxide compound (E)

$$A_1 + E \underset{K_-}{\overset{K_+}{\rightleftharpoons}} (A_1E), \qquad (7)$$

and as a nucleophilic reagent

$$(A_1E) + A_1 \xrightarrow{K_1} A_2 + A_1,$$

are a result of which an addition product (A_2) is obtained.

The decrease in the order of reaction with respect to amine in the presence of hydroxyl-containing impurities is related to its taking place partly by a catalytic mechanism, when the hydroxyl-containing compound, which is considerably more acidic than the amine, acts as a proton donor. It should be noted that in the usual method of purification of the reactants and the vessels used, the content of moisture in the reaction mixture is still sufficiently high and the order of reaction with respect to amine is considerably different from quadratic.[23,24] Thus, it was shown by Mutin et al.[25] that the reaction of PGE with butylamine has a fractional order ($1 \leqslant n \leqslant 2$) that is dependent on the reaction temperature. This case is effectively represented if account is taken of the fact that two reactions are taking place simultaneously in the system—one that is first-order with respect to amine (catalytic reaction) and one that is second-order with respect to amine (non-catalytic reaction). The

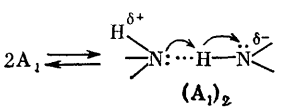
† Not only monomeric but also associated forms of hydroxyl-containing compounds and amines can act as proton donors and nucleophilic reagants.

contribution of each of these to the apparent rate is dependent on temperature, since their energies of activation are different, and on the concentration of the proton-donating impurities.

We should note that on the whole there are no fundamental differences‡ between the catalytic reaction, when activation of the epoxide ring is effected by the hydroxyl-containing component, and the non-catalytic reaction, where the amine itself acts as an electrophilic reagent (proton donor). It is important to note that electrophilic assistance is needed for opening of the epoxide ring by such weakly nucleophilic reagents as amines. This conclusion was also extended to other known nucleophilic addition reactions to an epoxide ring,[13] and it is essential for an understanding of the kinetic mechanisms of such processes.

Let us examine in greater detail the mechanism of addition of amines to the epoxide ring. The catalytic addition of amines takes place in two stages: initial formation of quite stable donor-acceptor complexes between the epoxide compound and the hydroxyl-containing reactant; and subsequent nucleophilic attack by amine on this complex, i.e., this quasi-termolecular reaction in fact comprises two successive bimolecular reactions with a push-pull mechanism occurring in the transition state. We should stress that in the donor-acceptor complexes between amine and hydroxyl-containing compounds ($A_i \ldots HOR$) formed in this process the amine is actually deactivated as a nucleophilic reagent and only free, uncomplexed molecules of amine act as the latter.

The question of the detailed mechanism of the non-catalytic reaction between epoxide compounds and amines still remains an open one. Apart from the mechanism shown in scheme (7), we can also put forward an alternative one which involves the initial formation of a more reactive amine dimer



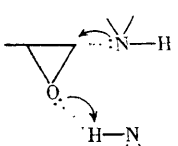
(8)

According to scheme (8) an increase in both the electrophilic and nucleophilic activity of the dimer compared to monomeric amine is to be expected. The kinetic scheme in this case can be given in the form:

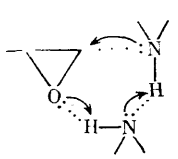
$$2A_1 \rightleftharpoons (A_1)_2,$$

$$(A_1)_2 + E \rightleftharpoons [(A_1)_2E] \rightarrow A_2 + A_1. \qquad (9)$$

The respective transition states for the alternative mechanisms (7) and (9) are shown in schemes (10) and (11):



(10)



(11)

‡ There is only a difference in the degree of activation of the epoxide ring.

It is impossible to distinguish between these mechanisms from the experimental data that are available at the present time. However, the second [scheme (11)] seems preferable to us, since according to this scheme addition of amine occurs via a cyclic transition state and is fully concluded in a single stage, whereas a further proton transfer is required in the realisation of scheme (9).

It is not excluded also that different mechanisms [see schemes (7) and (9)] can precede formation of the same transition state [see scheme (11)]. The question of the nature of the transition state in nucleophilic addition of an amine to an epoxide ring will be considered in greater detail below.

The kinetics of the condensation of primary and secondary amines with epoxides are well represented if account is taken of the fact that the main characteristic of these processes is the formation of different hetero- and auto-complexes that have varying reactivity. An interpretation of the physical significance of the apparent values of the termolecular rate constants that are determined still remains very approximate. This situation is evidently typical for liquid-phase reactions, in which different donor-acceptor interactions of all the components of the reaction system play an important part. For example, even the simplest non-catalytic reaction (in the absence of proton donors) of an epoxide compound with an amine should in general be given by a kinetic scheme that takes into account all the donor-acceptor interactions:

$$A_i^1 + A \underset{a}{\overset{K'_{ai}}{\rightleftharpoons}} A_{i+1}^1,$$

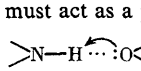
$$A_i^1 + A \underset{b}{\overset{K''_{ai}}{\rightleftharpoons}} (A_iE),$$

$$A_i^1 \underset{c}{\overset{K'''_{ai}}{\rightleftharpoons}} A_i^c,$$

$$A_i^1 + A_i^1 \xrightarrow[d]{K_{ij}} \text{product} + A_{i+j-1}^1, \qquad (12)$$

where A is a primary or secondary amine, the superscripts "l" or "c" indicate linear (reactive) and cyclic (non-reactive) autoassociates respectively. For reactions *a*, *b*, *d*: $i = 1, 2, 3, \ldots$; for reaction *c*: $i = 2, 3, \ldots, j = 1, 2, 3, \ldots$; K''_{ei}, K'_{ei}, K_{ei} are the equilibrium constants; k_{ij} are the true rate constants.

When glycidyl ethers are used as the epoxide compound and the solvent is electron-donating, kinetic scheme (12) will be supplemented by reactions involving complexation between amines and the non-ring oxygen atom in the glycidyl ether molecule and the electron-donating atom of the solvent molecule. In this case the amine must act as a proton donor



(13)

The apparent experimental rate constant of the non-catalytic reaction k_1 is determined from the equation

$$W_0 = k_1 E_0 A_0^2, \qquad (14)$$

where W_0 is the initial rate of reaction, A_0 and E_0 are the concentrations of the respective functional groups: the index "0" relates to the values of the parameters when $t = 0$.

From kinetic scheme (12) the following expression can be derived:

$$W_0 = \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} k_{ij} (A_i^1 E) A_j^1, \qquad (15)$$

where (A_i^1E) and A_j^1 are the equilibrium concentrations of the respective complexes. A solution to this equation, namely, a determination of the composition of the apparent rate constant in general form does not seem possible.

In reality the situation is of course simpler, since the concentration of all the complexes rapidly decreases with an increase in the degree of autoassociation. With regard to the relationship $k_{ij} = f(i, j)$, it can turn out to be non-monotonic since opening of the epoxide ring will occur with the greatest probability via a cyclic transition state that is dependent on the values of i and j.

At the present time a definitive answer to the problem concerning the composition of the apparent rate constant in opening of the epoxide ring by amine is not known. As a first approximation the autoassociation reactions of amine can be neglected. In this case the form of the expression for the apparent rate constant of the non-catalytic reaction assuming that $(A_1E) \ll E_0$ is quite clear [see scheme (7)]:

$$k_{app} = k_{tr}K_e, \tag{16}$$

where k_{tr} is the rate constant for the fundamental reaction of opening the epoxide ring [see schemes (10) and (11)], K_e is the equilibrium constant of the reaction $A_1 + E \rightleftarrows (A_1E)$.

The composition of k_{app} will also be similar if it is assumed that the reaction occurs by scheme (9) via a cyclic transition state [see scheme (11)]. Here K_e is the equilibrium constant of the reaction $2A_1 \rightleftarrows (A_1)_2$, in which $A_{1_0} \gg 2(A_1)_2$ and cyclic forms of the dimers are absent.

The treatment given above indicates that we encounter considerable difficulties in interpreting the physical composition of the apparent rate constant, which are related to the absence of valuable quantitative information on the thermodynamics of the reactions for formation of H-complexes and their reactivity. Further detailed studies of the donor-acceptor interactions in these systems would make it possible to find a more precise solution to this problem than we can offer at the present time.

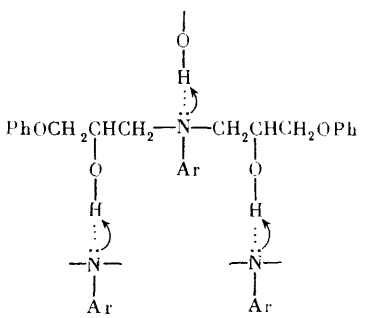
The question of the balancing mechanism which was touched upon above is very closely associated with the problem of the composition of the apparent rate constant. Without establishing this mechanism it is impossible to understand why in a complex system such as the epoxyamine system in question, where many donor-acceptor interactions take place and the reactivity of the H-complexes varies considerably, comparatively simple kinetic mechanisms occur. These are namely: a slight dependence of the apparent rate constant on the degree of conversion, simple dependences of the initial rate on the concentration of reactants, a linear dependence of the total quantity of liberated heat Q on the degree of conversion, and the similarity between the values of Q and the enthalpy for opening the epoxide ring. The latter two problems have been discussed already and the essence of the first two can be revealed, for example, in a study of the non-catalytic reaction.

According to kinetic scheme (12), the initial rate of reaction will decrease compared to that which would occur in the absence of any donor-acceptor interactions as a result of a decrease in the total number of nucleophilic species due to autoassociation of the amino groups and will increase because of an increase in the nucleophilicity of the associated amino groups as well as a certain increase in acidity of the auto-complexes of amine (compared to that for unassociated molecules). This combination of positive and negative factors should lead to a certain levelling out of the role of donor-acceptor interactions in changing the concentrations of reactants and reaction products, namely, a balancing effect. The linear dependence between the current reactant concentrations and the concentrations of their free, uncomplexed forms can also be attributed to its occurrence. In general the magnitude of the balancing effect depends on the nature of the reactants and the specific reaction conditions.

One of the kinetic manifestations of the formation of H-bonds in an epoxyamine system is shown not only in an acceleration but also a deceleration of this reaction at its advanced stages.

The deceleration effect of the advanced stages of conversion is due to the formation of unreactive complexes (A_iH_n). Complexation, on the one hand, reduces the concentration of the reactive complex (EH_n) and, on the other hand, reduces the concentration of free amine and hence leads to a retardation of the process. It should be stressed that deceleration of the reaction can only occur when the basicity of the resulting secondary of tertiary amino groups (or of both of them) is greater than the basicity of the initial primary amino group. Only in this case will a progressive relative decrease in the concentration of free hydroxyl groups, and hence in the rate of overall process, occur.[13,19,20,30]

Complexation of the amino groups with the hydroxyl groups is clearly revealed in the fact that the viscosity of the reaction system at the advanced stages of the processes increases substantially as a result of the formation of a network with labile hydrogen bonds at branch points, since the formation of tertiary amino groups gives rise to a trifunctional reaction occurring in the system (one tertiary amino group and two hydroxyl groups):



(17)

In complete agreement with what is expected, the effect of an increase in viscosity of the system during the reaction increases with a decrease in the ratio of A_{1_0}/E_0, where the index "0" denotes the concentrations of reactants at an initial point in time. In this case the maximum attainable value of the viscosity increases. Thus, when A_{1_0}/E_0 = 1.8; 1.0; 0.45, $\eta_{rel\,t\to 0}$ = 3.5; 14.0; 32.5 respectively. Introduction of a stronger base into the reacting system causes a sharp decrease in viscosity of the system as a result of break-up of the polyfunctional associates.

An increase in reaction temperature leads to a decrease in the proportion of amines associated with hydroxyl groups, and as a result to inhibition of the process starting to occur at a more advanced stage. When the reaction is carried out under adiabatic conditions, 100% conversion of the epoxide groups is achieved without any autoinhibition effect.[23]

Thus, the hydroxyl group has a dual role in this reaction. On the one hand, it leads to considerable activation of the epoxide ring as a result of the formation of a complex (EH_n); on the other hand, in the formation of unreactive complexes (A_iH_n) the rate of reaction is reduced because of a decrease in the concentrations of primary and secondary amines as well as that of free hydroxyl groups not forming (A_iH_n) complexes and which catalyse the reaction. The second factor, naturally, has a much greater effect in reducing the

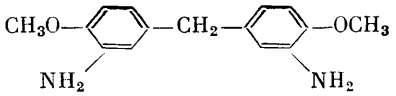
rate than does the first, which is also borne out by the experimental results.[20,30] Additions of a model secondary alcohol—cyclohexanol—lead not only to an increase in the rate of reaction but also to an increase in the degree of conversion at which a marked inhibition of the reaction occurs.

Thus, the results presented above suggest that the mechanism of the reaction of epoxide compounds with amines makes it basically possible for not only autocatalysis but also an autoinhibition effect at advanced stages of the reaction to be exhibited in such systems. However, the latter can only occur when the relative concentration of free hydroxyl groups decreases during the reaction because of the increase in the equilibrium constant for complexation between a hydroxyl group and an amino group on changing from a primary amino group to a secondary and then tertiary amino group.

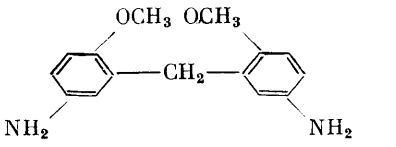
When electrophilic assistance reagents are introduced into the epoxyamine systems (alcohols, phenols, carboxylic and Lewis acids) in order to activate the epoxide ring, donor-acceptor interactions can cause a dual kinetic effect—both acceleration and inhibition of this reaction depending on the concentration and acidity of the added components.[13,64,65] When activators with quite a high acidity are used (carboxylic and Lewis acids), the dependence of the rate of reaction on the concentration of added component is extremal in nature.

Actually the effect of activating the epoxide ring towards a reaction with nucleophilic reagents increases with an increase in acidity of the electrophilic assistance reagent. At the same time an increase in the acidity and concentration of the added component leads to the amine being bound in an unreactive complex right up to complete inhibition of the reaction when all the amine is bound. This effect is sometimes used to regulate the rate of curing of such systems. These so-called latent systems have considerable viability at low temperatures but start to react at a high rate on heating, which results in decomposition of the unreactive amine–acid complexes.[13]

Consideration of donor-acceptor interactions also makes it possible to understand the kinetic effects related to the structure of the initial reactants. There are a number of facts which attest to the anomalously low reactivity of aromatic amines containing electron-donating groups at the *ortho* position. Thus, the reactivity of an amino group which has SCH_3 as the *ortho* substituent is 21 times lower than for an amino group without this substituent.[56] A similar pattern occurs for aromatic amines with methoxyl groups at the *ortho* position.[37]



(18)

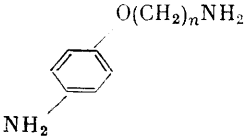


(19)

The reactivity of diamine (18) when it reacts with resorcinol diglycidyl ether is approximately 10 times lower than for (19). For both amines containing electron-donating substituents at the *ortho* position the presence of an intramolecular hydrogen bond in which the amine group acts as a proton donor has been established. It would appear that the nucleophilicity of this amino group must increase as a result of both the inductive effect of the electronic substituent and through the formation of an intramolecular donor-acceptor complex, although in reality it decreases. This contradiction can be readily eliminated if it is borne in mind that the hydrogen atoms of the amino group are involved in formation of an associate, namely, the concentration of amine as a proton donor in the reaction system decreases. It is evident that in terms of the ideas being developed concerning obligatory electrophilic assistance for nucleophilic attack on the epoxide ring, this reduction in concentration of proton donors in highly pure systems (when the amine itself acts as a proton donor at the initial stage of the reaction) must lead to a decrease in the rate of reaction. This is what actually occurs.

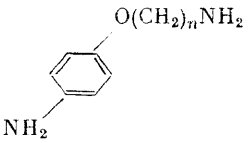
On the basis of the ideas put forward above, a whole series of aliphatic and mixed (aliphatic-aromatic) liquid oligomers with reduced reactivity was synthesised:[41]

$$ArNHCH_2CH_2(OCH_2CH_2)_mNH_2 \ (m = 1, 2), \tag{20}$$



(21)

$(n = 2,3)$

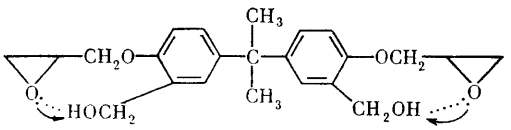


(22)

The use of such amines as curing agents has considerable technological advantages, increasing the viability of composite materials.

The high reactivity of *o*-diglycidyl ethers of phenols, *o*-diglycidyl esters of aromatic carboxylic acids, and *N*-diglycidylamines can only be explained by assuming that secondary hydroxyl groups, which are present in these compounds as small quantities of impurities, participate in catalysis.[13,43,44,66–67]

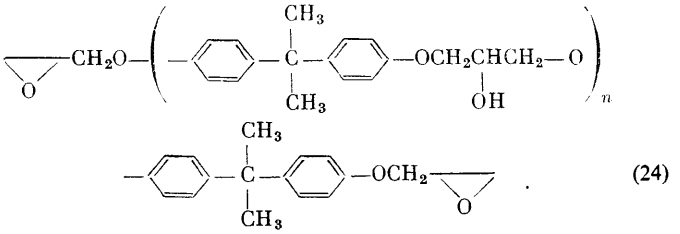
The presence of intramolecular hydrogen bonds in the 3,3′-dihydroxymethyl-4,4,′-diglycidyl ether of bisphenol A



(23)

gives rise to its considerably higher reactivity (by a factor of about 10) than that of the diglycidyl ether not containing hydroxymethyl groups at *ortho* positions.[68]

The rate of curing the epoxybisphenol A oligomers (24) increases with an increase in molecular weight of the oligomer, although the concentration of the epoxide groups decreases as this occurs.[13,20,29,45] This result, which appears paradoxical at first glance, is quite obvious when it is borne in mind that with an increase in molecular weight of the oligomer there is an increase in concentration of hydroxyl groups, which leads to an increase in the rate of reaction



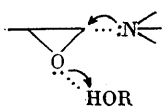
(24)

Determination of the reactivity of the epoxide groups in oligomers with varying molecular weights (taking into account the concentration of the hydroxyl groups contained in them) showed that it is the same and does not depend on the molecular weight of the oligomer.

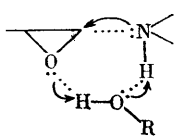
Even in early studies on reactions of epoxides with amines[56–63] it was noted that both proton-donating and electron-donating solvents have a considerable effect on the reaction kinetics. Proton-donating solvents decrease the induction period and increase the rate of reaction to a greater extent the higher the acidity of the solvent, whereas electron-donating solvents reduce both the initial and continuing rate of reaction, and as the degree of conversion of the epoxide groups increases, the inhibition effect increases.[19,20,37,39,40] This type of solvent behaviour is fully consistent with the reaction mechanism considered above. The inhibitory effect of electron-donating solvents is caused by the reduction in concentration of proton donors in the reaction system as a result of their bonding with solvent molecules. At the initial stage amines are bound by solvent while during the reaction hydroxyl groups are bound.[37]

The rate of reaction in strongly associated systems can easily vary over quite a considerable range from the effect not only of the solvent but also of other factors such as temperature and external mechanical or electrical fields, which are capable of changing the degree and nature of association of the reacting groups.[13,69–71]

In concluding this section let us return to the question of the mechanism of addition of amines to an epoxide ring. Possible transition states for non-catalytic opening of the epoxide ring by amine are depicted in schemes (10) and (11). Such schemes can similarly be recorded for a reaction catalysed by any proton donor, such as ROH:



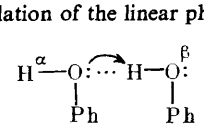
(25)



(26)

It does not appear possible to distinguish these two alternative schemes from the existing kinetic and structural data. At the same time, from detailed kinetic and structural studies of certain other nucleophilic addition reactions to the epoxide ring (phenols and carboxylic acid) it is possible to choose in favour of a cyclic transition state [scheme (26)].[13,46–48]

In the reaction between PGE and phenol[46] a variable order of reaction with respect to phenol was found; at small phenol concentrations it was close to first order, while at large concentrations it increased to fourth order. High values for the order of reaction with respect to the hydroxyl-containing reagent were also obtained in addition of alcohols to propylene oxide[72] or isocyanates,[3] which is due to an increase in reactivity of the hydroxyl-containing compounds on forming autoassociates. A quantum-mechanical calculation of the linear phenol dimer



(27)

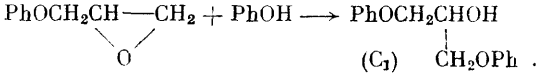
revealed a considerable reduction in electron density on the H^{α} hydrogen atom and an increase in electron density on the O^{β} oxygen atom compared to "monomeric" phenol.[73] Naturally this must result in an increase in proton-donating capacity and nucleophilicity of the phenol dimer. Such changes in the distribution of electron density are even more typical for higher molecular-weight associates.

Taking into account the different possible homo- and hetero-associates, the initial rate of the reaction between phenol (P) and epoxide (E) can be satisfactorily represented by the following simplified scheme, which assumes that all phenol autoassociates have solely a linear structure,

$$P_{i-1} + P \overset{k_i}{\rightleftharpoons} P_i, \quad E + P_i \overset{K_{1i}}{\rightleftharpoons} (EP_i),$$

$$(EP_i) \xrightarrow{k_i} C_1 + P_{i-1}, \qquad (28)$$

where C_1 is the primary product of the addition of PGE to phenol

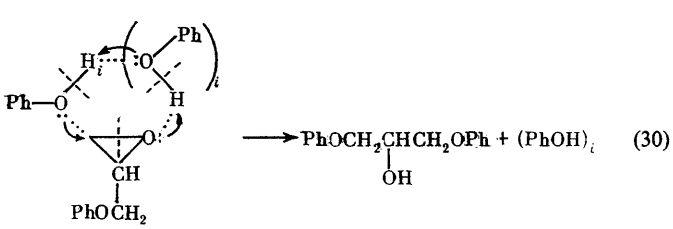


(29)

K_i and K_{1i} are the equilibrium constants for the respective reactions, k_i are the rate constants for formation of C_1.

The unimolecular conversion of the heteroassociates (EP_i) to the reaction product in accordance with scheme (28) in essence assumes a cyclic transition state. The values of the kinetics parameters determined from this scheme showed that the rate of formation of C_1 is mainly determined by processes involving association of the epoxide with higher forms of phenol associates (P_4 and P_5).

The revelation of the determining role of phenol associates can only be understood in terms of kinetic scheme (28), which assumes the unimolecular decomposition of heteroassociate (EP_i) via a cyclic transition state which is more probable sterically for H-complexes of PGE with higher forms of phenol associates.

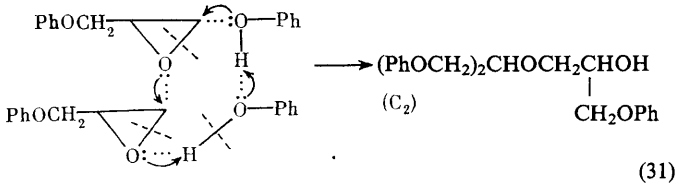


(30)

In the transition state the donor-acceptor bonds indicated by arrows are converted into covalent bonds, while the covalent bonds that are intersected by broken lines are cleaved synchronously to form the final reaction products. The formation of the transition state, which comprises a complex cyclic heteroassociate, is preceded by the process of "assembling" its individual fragments, each of which is a simpler homo- or hetero-associate. In this case the principal determining reaction channel, as kinetic studies have shown, is provided by heteroassociates (EP_i), where $i = 4, 5$.

In achieving a cyclic transition state the formation of reaction products occurs simultaneously with the transfer of a proton from the nucleophilic reagent to the molecule which provides electrophilic assistance. In this case the latter essentially fulfils two functions: it activates the epoxide ring towards nucleophilic attack and increases the activity of the nucleophilic reagent, i.e., bifunctional catalysis takes place and a "push-pull" reaction mechanism occurs. It is evident that such a mechanism predicates a lower energy of activation of the reaction than for a non-cyclic transition state, but imposes stricter limits on the entropy factor.

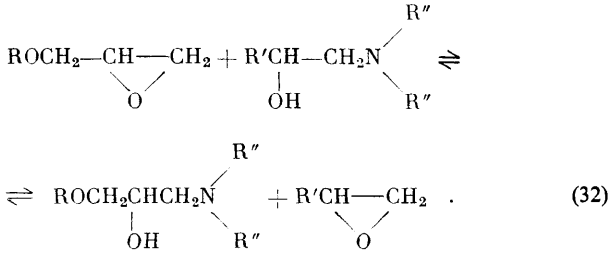
Using the concept of a cyclic transition state it is possible to understand the fact of parallel formation of a secondary addition product (C_2) directly from the initial reactants.[74] This reaction can be depicted as follows:



(31)

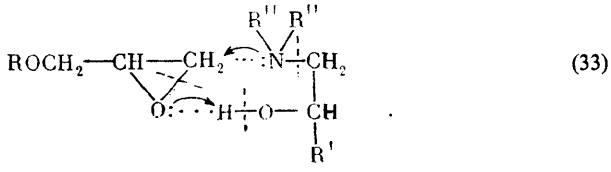
The formation of this type of transition state is evidently preceded by the development of simpler heteroassociates of the type (EP). It is interesting to consider the fact that kinetic studies demonstrate that in all only two molecules of phenol take part in this reaction, and not more as in the formation of C_1.

In fact, similar results were also obtained in the reaction between epoxide compounds and carboxylic acids.[47] Lastly, we shall give two final examples. A novel reaction, namely, amino alcohols on reacting with epoxide compounds can undergo transepoxidation, was recently discovered:[49]



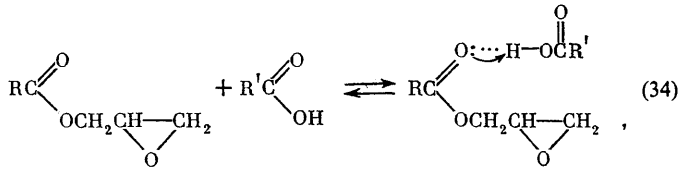
(32)

Evidently the most probable mechanism for this is given by the following:



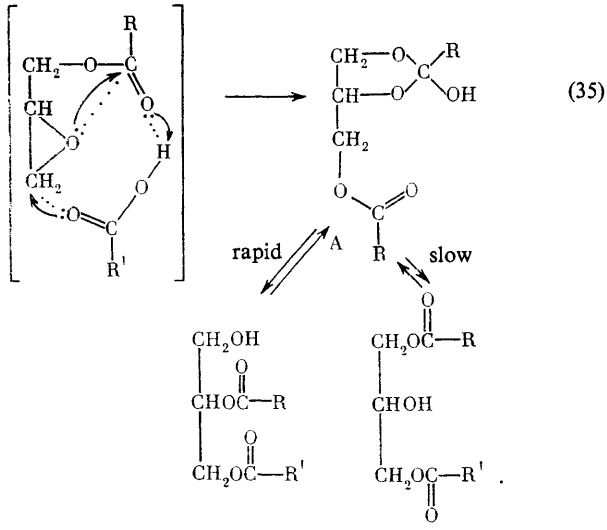
(33)

Without involving the concept of a cyclic transition state it is also impossible to understand the reaction between carboxylic acid glycidyl esters and carboxylic acids, which results in the formation of an "anomalous" addition product;[74] whereas in the reaction between phenol glycidyl ethers and carboxylic acids, "normal" addition products are obtained. In the first case the product of the donor-acceptor interaction between the hydroxyl group of the acid and the carbonyl group of the ester will evidently become an "active" complex:



(34)

which forms a cyclic transition state



(35)

From the scheme presented it is possible to understand not only the formation of the "anomalous" addition product but also the subsequent slow conversion of the latter to the more stable "normal" addition product via the intermediate A.

Thus, the examples of model reactions for the curing of epoxide oligomers considered above indicate that addition of nucleophilic reagents to the epoxide ring occurs in a very complex manner and involves the initial formation of homo- and hetero-associates. The latter in turn can form even more complex reactive cyclic heteroassociates that act as unique microreactors in which the reaction products are obtained through unimolecular rearrangement with synchronous transfer of electrons in the system.[1–4,13]

The presence of a cyclic transition state is very typical of a large number of reactions in the liquid phase in which various donor-acceptor interactions between the components of the system are possible.[55] The structural organisation of this type of reaction system caused by the donor-acceptor interactions of its components (initial reactants and reaction products) governs, on the one hand, the multiplicity of the routes for passage of the reaction and, on the other hand, the few routes for its favourable development.

Further studies directed at finding a link between the kinetic mechanisms of the chemical reactions and the structural organisation of liquid-phase systems involving polar reactants should lead to a re-examination of the mechanism of many reactions which seem to us at the present time to be well studied.

IV. Donor-acceptor interactions and polymer structure

The donor-acceptor interactions which exist in the reaction system not only govern the kinetic mechanism of the process but also can affect the structure of the resulting polymer in individual cases. Thus, the topological structure of an epoxyamine cross-linked polymer depends to a considerable extent on the occurrence of ineffective cyclisation reactions during its derivation, which lead to the formation of so-called monocycles that in the final analysis reduce the concentration of elastically active chains of the network.[13,15,31,44] The proportion of such ineffective rings is

determined by the ratio of rate constants of intra- and inter-molecular reactions, which in turn depends on the ratio of intra- and inter-molecular hydrogen bonds in diepoxides.

It has been shown in a considerable number of studies[13-16,31,43,76-82] that the *o*-diglycidyl esters of diphenols or *o*-diglycidyl esters of aromatic dicarboxylic acids and also *N*-diglycidylamines have a considerable tendency to form ineffective rings. An important factor that assists the development of ineffective rings in these cases is the formation of a strong intramolecular bond in the products of the primary addition of amine to diepoxide, resulting in activation of the neighbouring epoxide group. The effect of increased reactivity of these diglycidyl ethers and the positive effect of substitution in these monomers are precisely related to this phenomenon.[13,43,44]

The formation of cross-linked polymers with a defect topological structure naturally has an effect on their physical and mechanical properties in the hyperelastic and vitreous states.[77-82] A number of interesting observations about the effect of donor-acceptor interactions on the structure and properties of the polymers formed are made in two studies concerning the processes for formation of polyurethanes.[83,84]

Thus, donor-acceptor interactions between the components of a reaction system during polycondensation processes to a considerable extent determine the reactivity of the resulting homo- and hetero-associates and, as a result, the mechanism of the fundamental stages of condensation and the kinetics of the process. In three-dimensional polycondensation, donor-acceptor interactions can have an effect on reactions leading to intramolecular cyclisation, resulting in the formation of ineffective rings, and hence on the structure and properties of the resulting cross-linked polymers.

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