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Some Problems of the Kinetics and Thermodynamics of Polymer Formation Reactions

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The characteristic features of the thermodynamics, kinetics, and mechanism of the ionic polymerisation of oxygen- and nitrogen-containing heterocycles as well as aldehydes are considered. The interchain exchange and polymerisation reactions under non-standard physical conditions are discussed.
The bibliography includes 155 references.

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I. INTRODUCTION

Compared with anionic[1] and cationic[2] polymerisation of vinyl monomers, ionic processes involving the formation of heterochain polymers exhibit considerable specific features. Many fundamental characteristics of these processes have been observed in the study of the kinetics of the polymerisation of cyclic acetals and ethers, nitrogen-containing heterocycles, and aldehydes, which are largely examined below. In order to understand the complex kinetics of the ionic polymerisation of heterocycles, it is necessary to take into account the active role of the macromolecules formed, which influence all the steps in the polymerisation process—the initiation of the growing active centres and the propagation, transfer, and termination of the reaction chains[3].

One of the distinctive features of ionic polymerisation is the multiplicity of types of active centres (free ions, contact ion pairs linked to different extents, covalent centres, solvate-separated ion pairs, ion triplets, etc.), which exist in equilibrium, different active centres exhibiting different reactivities[1,4]. When the counterions are in addition linked to one another via the bond system of the polymer chain, a special type of ionic polymerisation arises—zwitterionic polymerisation characterised by specific kinetic and thermodynamic features.

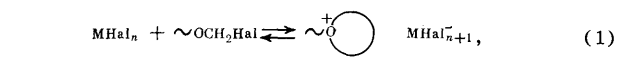
The thermodynamic parameters of polymerisation have been used traditionally to analyse the possibility of the conversion of a given monomer into a polymer. An important step towards the understanding of the general characteristics of polymerisation has been the determination of a relation between the kinetics and thermodynamics of heterophase polymerisation. The development of ideas concerning the dependence of the reactivity of the active centres on their phase state made it possible to explain the kinetics of the polymerisation reaction in which the polymer constitutes a separate phase.

This review deals with problems of the influence on the polymerisation kinetics of factors such as pressure, electric field, and other physical process conditions. The studies by N.S.Enikolopov included in the present review were completed mainly towards the 1970s, but they yielded many fundamental results which have exerted and continue to exert a significant influence on the development of the field under consideration.

II. CATIONIC POLYMERISATION OF HETEROCYCLES

Among the heterocyclic monomers polymerised via a cationic mechanism, cyclic acetals proved to be an extremely unusual class of monomers. The majority of the reactions in which acetals can participate are characteristic also of ethers, but the reactivity of the former is so much greater that the difference between them assumes a qualitative character. In particular, owing to the different reactivities of the acetal and ether linkages, the opening of the acetal ring in polymerisation takes place exclusively at the acetal linkage.

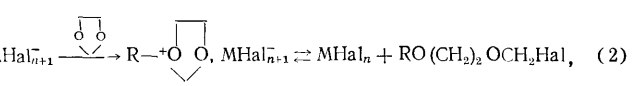
Accordingly, cyclic acetals should be much more reactive in polymerisation than, for example, tetrahydrofuran. In practice, the behaviour of cyclic acetals is much more complex: depending on the type of cationic catalyst, the rate of their polymerisation can be much greater than, similar to, or even lower than that of cyclic ethers. Tetrahydrofuran polymerises in the presence of different catalysts with similar process rate constants, while the effective rate constants for the polymerisation of 1,3-dioxolan in the presence of the same catalysts vary almost by four orders of magnitude[5]. The cause of this anomaly is associated with the influence of the nature of the counterion on the overall concentration of active centres: the following equilibrium plays the most important role in the establishment of the concentration of the active centres[5-12]:



$$MHal_n + \sim OCH_2Hal \rightleftarrows \sim \overset{+}{O} \bigcirc \quad MHal_{n+1}^-, \qquad (1)$$

where M is the metal (Sb, Sn, etc.) and Hal is the halogen. Other possible causes, namely the influence of the counterion on the state of the ions $\rightleftharpoons$ ion pairs equilibrium or the direct influence of the counterion on the reactivity of the active centres in the form of ion pairs, do not contribute significantly to the rate of reaction.

In many instances, an additional decrease in the concentration of the active centres associated with slow initiation is observed:



$$R^+MHal_{n+1}^- \rightarrow R-{}^+O\bigcirc O, \; MHal_{n+1}^- \rightleftarrows MHal_n + RO(CH_2)_2OCH_2Hal, \qquad (2)$$

where R^+ is the cation of the initial salt.

Reactions (1) and (2) naturally do not exhaust all the different versions of the formation of active centres with reversible decomposition of the counterion; in the general case there is a possibility of a set of compounds of the type $MHal_{n-k}(^{\sim}OCH_2)_k$, where $k \leq n$, with the corresponding counterions $[MHal_{n-k+1}(^{\sim}OCH_2)_k]^-$. A spectroscopic confirmation of this fact has been described[13].

An important consequence of the decisive role of equilibria of type (1) is effective cocatalysis when substances which are ineffective as catalysts but can displace equilibrium (1) towards the active centres are introduced into the system (Table 1).

Table 1. The influence of the concentration of the added α-chloromethyl ether (c) on the rate (w) of the dissociation reactions of the acetal linkages*.[5,6,12]

Catalyst	$10^4 c$**, mole %	w/w_0***
Polymerisation of 1,3-dioxolan		
$(C_2H_5)_3O^+SbCl_6^-$	1.6	300
$SbCl_5$	0.7	190
$Ph_3C^+SbCl_6^-$	2.2	90
Methylal + ethylal model system		
$(C_2H_5)_3O^+SbCl_6^-$	7	25
$SnCl_4$	2	25

*Solvent—CH_2Cl_2; 20 °C.

**The concentration of the additive relative to the amount of the catalyst.

***Here w_0 is the rate of reaction in the absence of additives.

Thus in the case of cyclic acetals a type of "living" polymerisation obtains where only a small proportion of macromolecules grow in each instant but the dynamic equilibrium (1) ensures the possibility of the growth of all the chains throughout the process. In contrast to the usual polymerisation via the "living" chain mechanism, in the case of acetals, the concentration of the growing macromolecules is determined by the constant of equilibrium (1) and by the equilibrium constants of the analogous interactions of the initial and substituted Lewis acids with the polymer chain. On the basis of these ideas, it has been possible to explain the linear growth of the molecular weight of the polyacetals as a function of the degree of conversion, observed in many instances, i.e. a constant number of chains, which, however, is not identical to the number of catalyst molecules and depends on the temperature and other process parameters[14].

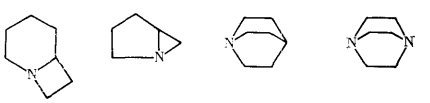
Later studies yielded convincing evidence showing that the equilibrium mechanism of the formation of ionic active centres plays an important role not only in the polymerisation of cyclic acetals but also in the cationic polymerisation of other heterocycles, particularly tetrahydrofuran[1,15-21].

The study of the polymerisation reactions of cyclic acetals permitted a significant step forward in the development of ideas concerning the relative reactivities of the free ions and ion pairs. The results of experiments designed to investigate the influence of the ionic strength of solutions and of the dielectric constant of the medium on the polymerisation process led to the conclusion that intense solvation of the cations by the monomers and delocalisation of the positive charge should equalise the reactivities of the free ions and ion pairs[22]. In contrast to the anionic polymerisation of vinyl monomers, the rate constants for the propagation of ions and ion pairs proved to be similar.

The initiation methods in the polymerisation of cyclic acetals are distinguished by a wide variety[4,5,23-33] in both the chemical and the kinetic sense. Depending on the reactivity of the active centres in relation to the acetal linkages and on the stability of the counterions, there is a possibility of the equilibrium[5,9,29,32], stationary[5], or mixed[5,10] initiation mechanisms. The case of the stationary mechanism, which obtains in the initiation of polymerisation by salts with fairly stable counterions, is extremely interesting; the initiation of the polymerisation of 1,3-dioxolan by the oxonium salt $(C_2H_5)_3O^+SbF_6^-$ can serve as an example of this kind[5].

The polymerisation of cyclic acetals is instructive also because many types of interactions characteristic of the cationic polymerisation of other heterocyclic monomers, for example, esters and ethers, are effectively realised in this process. The systems considered are characterised by a high sensitivity to the presence of microamounts of nucleophilic impurities (water, alcohols, etc.), the involvement in various stages of the reaction of not only the initial monomer but also of other heterocycles formed from the polymer chain via a depolymerisation mechanism, and the effective formation of complexes between different system components[34-46]. The proof of the fact that the polymer molecules are capable of participating, together with the monomer, in the formation of complexes with the catalyst and also in initiation, in reactions with the impurities, etc. was extremely important for the understanding of the experimental kinetics in the systems considered[34-36].

The cationic polymerisation of oxygen-containing heterocycles has much in common with the analogous processes involving many cyclic amines: 1-azabicyclo[4.2.0]octane (conidine), 1-azabicyclo[3.1.0]hexane (ABH), 1-azabicyclo[2.2.2]octane (quinuclidine), and 1,4-diazabicyclo.[2.2.2]octane (triethylenediamine):[47-49]



conidine ABH quinuclidine triethylenediamine

Table 2. The chain propagation rate constant (k_p) in the cationic polymerisation of conidine and the influence of catalysts of different types*.[47,48]

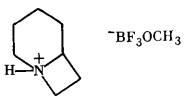
Catalyst	Concentration, M	k_p, litre mol^{-1} min^{-1}
BF_3-conidine	$5 \cdot 10^{-3}$	0.29
Ditto	$1 \cdot 10^{-2}$	0.48
Conidine hydrobromide	$5 \cdot 10^{-3}$	0.23
Ditto	$6 \cdot 10^{-2}$	0.38
N-Ethylconidinium iodide	$1 \cdot 10^{-2}$	0.21
Ditto	$6 \cdot 10^{-2}$	0.59

*Solvent—methanol; 60 °C.

The nature of the active centres for the polymerisation of cyclic amines is the same and is independent of the type of initiator: the active centres are quaternary ammonium salts. This is indicated, in particular, by the finding that the

chain propagation rate constant is independent of the nature of the initiator at the concentration of the active centres corresponding to their virtually complete dissociation into the free ions (see Table 2).

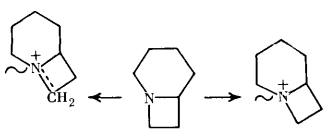
The structure of the initiating species in the conidine–CH_3OH–BF_3 system has been unambiguously established by ^1H, ^{11}B, and ^{19}F NMR.[49]



In virtually all cases the polymerisation of nitrogen-containing heterocycles is a process without termination, which proceeds via a mechanism of the "living" polymer type. In initiation by alkyl halides or quaternary ammonium salts, the rate of initiation is fairly high and the reaction takes place without an induction period and without self-acceleration. The molecular weight of the polymer increases in proportion to the initial monomer concentration and the degree of conversion and is independent of temperature, the monomer concentration, and the nature of the counterion. In the polymerisation of nitrogen-containing rings under the influence of acids, tertiary ammonium salts, and BF_3–monomer complexes, all the kinetic features fully agree with the mechanism involving a slow initiation stage. In conformity with this mechanism, the number-average degree of polymerisation $\bar{P}_n$ increases in proportion to the square root of the degree of conversion[5].

It is of interest to note the similarity between the nitrogen- and oxygen-containing rings in the sense that the tertiary ammonium ions used as catalysts react much more slowly with their monomers than R_4N^+, completely analogously to the mechanism of the inhibiting action of water in the polymerisation of oxygen-containing rings, where tertiary oxonium ions R_3O^+ are converted into the relatively inactive secondary ions R_2OH^+.

The available data show that the chain propagation in the polymerisation of cyclic amine proceeds via the nucleophilic attack on the active centre by the monomer; for example, in the case of conidine (the counterion is omitted) we have



The structure of the initial ring is retained in this process, while the reactivity is determined mainly by the ring strain[49].

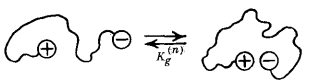
Conductimetric studies of ammonium salts in polymerising systems, experiments with added neutral salts, and the study of the influence of the nature of the counterion on the reaction kinetics suggest that the active centres in the polymerisation of nitrogen-containing rings are free ions and ion pairs[48]. The decisive argument in support of this conclusion is the change in the rate of polymerisation and the influence of neutral salts which suppress the dissociation of ion pairs and shift the equilibrium ions $\rightleftharpoons$ ion pairs towards the latter. In contrast to the majority of the data available at present, the rate of polymerisation increases in this instance, since ion pairs are more active than the free ions in the polymerisation of the cyclic amines investigated and the greater the size of the counterion the higher the rate constant for the propagation of the macroion pair. The size of the cation has an analogous influence on the process kinetics: the ratio of the rate constants for the propagation reactions involving the ion pair and the free ion is greater for a four-membered ring than for a three-membered ring in the presence of the same counterion.

The conclusion that the reactivities of the free ions and ion pairs in the polymerisation of cyclic amines are similar was confirmed later in studies by other workers[50]. A similar situation is typical for the cationic polymerisation of many other heterocycles, for example, tetrahydrofuran, oxepan, and sulphur-containing monomers[4,5].

III. ZWITTER-IONIC POLYMERISATION

In the ionic polymerisation of vinyl monomers and heterocycles, the mechanism by which the active centres formed by the ions are linked to one another solely by electrostatic interaction forces is most frequently encountered. However, there is a possibility of ways of initiating polymerisation in which dipolar active species (zwitter-ions) are formed and the subsequent growth of the polymer molecule takes place via the addition of the monomer molecules to the cation (cationic mechanism) or the anion (anionic mechanism); the anion and cation are then on the opposite ends of the polymer chain. The addition of monomer molecules does not alter the zwitter-ionic nature of the active centres and is accompanied by an increase of the number of covalent bonds between the oppositely charged groups.

A statistical description of the behaviour of the macromolecule in solution is based on the idea of a Gaussian coil, the average distance between the ends of which increases with increase of the chain length. In the case of a polymer zwitter-ion, the electrostatic interaction between the charges at the ends of the chain should lead to their mutual approach and the formation of an ion pair:



However, such a change in the coil conformation is accompanied by a decrease of the entropy of the macromolecule.

Allowance for the configurational statistics of the polymer chain and the law of electrostatic interaction between the charges of the polymer zwitter-ion made it possible to obtain an expression for the equilibrium constant of the dissociation of an isolated polymeric zwitter-ion as a function of the degree of polymerisation n:[52,53]

$$K_g^{(n)} = K_g^{(1)} n^{3/2},$$

where $K_g^{(1)}$ is a constant which depends solely on the thermodynamic flexibility of the chain. In contrast to the usual dissociation of electrolytes, including polymeric electrolytes, the dissociation constant of the growing zwitter-ion depends on its length and the probability of finding an active centre in the form of a free ion increases with increasing degree of polymerisation of the zwitter-ion. If the reactivities of the free ions and ion pairs are different and the former are more reactive, then the rate of growth of the polymeric zwitter-ion should increase with increase of its length. This fact, which is fundamentally new in polymer chemistry, seemingly contradicts Flory's fundamental postulate that the reactivity of the active centres is independent of the length of the macromolecule; however, in reality there is no contradiction here: the reactivities of the ion pairs and the free ions are independent of the length of the macromolecule and there is only a change in the probability of the existence of the active centres in these states.

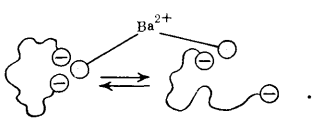
The anionic zwitter-ionic mechanism obtains in the polymerisation of acrylonitrile and its derivatives, β-propiolactone, and formaldehyde under the influence of triethylphosphine as the initiator and of ε-caprolactone and cyclic sultones under the influence of tertiary amines[54–67]; one of the examples of the cationic zwitter-ionic polymerisation is that of epoxides under the influence of BF_3.[68,69]

Another characteristic feature of the zwitter-ionic polymerisation initiated by triethylphosphine is the slow accumulation of ions in the system during the reaction which is due to the slow initiation. The increase of the overall concentration of ions owing to the initiator which has reacted leads to the suppression of the dissociation of the polymeric zwitter-ions via mechanism (3).† The decrease of the concentration of the free anions active in polymerisation also takes place owing to their interaction with the cations of the chains which have been destroyed. Since the ion pairs in the test systems are less reactive than the free ions, the suppression of polymerisation and even its complete arrest, unrelated to the exhaustion of the reactants, are observed during the process. The introduction of a fresh portion of the initiator does not then renew the polymerisation process.

The influence of these factors on the process kinetics has been analysed in relation to the anionic zwitter-ionic polymerisation of methacrylonitrile under the influence of $(C_2H_5)_3P$: the rate of polymerisation and the molecular weight of the polymer decrease during the process faster than would be expected solely from the decrease of the concentrations of the reactants[57,58].

An important kinetic consequence of the zwitter-ionic mechanism of polymerisation is the broadening of the molecular weight distribution (MWD) within the polymers with increase of the concentration of the monomer as a result of a sharp increase of the contribution of the free ions to the polymerisation with increase of the molecular weight of the growing polymer chain.

The ideas developed above concerning the specificity of the growth of the active centres in the form of zwitter-ions were extended subsequently to the anionic polymerisation of styrene under the influence of dianions combined with Ba^{2+} as the counterion: in this case the active centre dissociates only once in tetrahydrofuran:



Chain propagation takes place mainly with participation of singly dissociated barium salts of polystyrene which are in fact zwitter-ions: it has been established that the effective propagation rate constant increases with increased degree of polymerisation, in full agreement with one of the fundamental features of the kinetics of the zwitter-ionic polymerisation[53,70-73].

IV. THERMODYNAMICS OF POLYMERISATION

The relation between the rate of the process w_p and the equilibrium monomer concentration [A] is well known for homogeneous polymerisation:

$$w_p = -\frac{d[A]}{dt} = k_p c^* ([A] - [A]_{lim}) , \qquad (4)$$

where $[A]_{lim}$ is the limiting, equilibrium concentration of the monomer, c* the concentration of the active centres, and k_p the propagation rate constant. This law obtains in the polymerisation of many unsaturated and cyclic monomers for which the enthalpy and entropy contributions to the free energy of polymerisation are comparable in magnitude. However, another form of the relation between the process kinetics and thermodynamics, which obtains in those cases where the polymerisation is reversible but the polymer forms a separate phase, as, for example, in the heterophase polymerisation of trioxane, escaped the attention of investigators[74-85].

In a polymerisation system of this type the growing macromolecule can be either fully crystallised, so that the active centre is located on the surface of the polymer crystal, or is partly dissolved in the reaction medium, whereupon the active centre is located at the end of the dissolved section of the polymer chain. The equilibrium monomer concentrations in relation to the polymer in the dissolved and crystalline states are different. The addition of the monomer to the surface active centre with formation of a solid polymer is thermodynamically more favourable, so that the equilibrium monomer concentration is in this case lower than in relation to the polymeric centre in solution.

Thus processes involving the addition of the monomer to the active centre at the dissolved end fragment of the macromolecule, the reverse reaction involving the depolymerisation of this section of the chain, chain propagation, the depolymerisation of the active centres on the surface of the crystal, as well as the crystallisation and dissolution of the growing chain takes place in the polymerisation system. The character of the dependence of the rate of reaction on the monomer concentration is determined by the ratios of all these processes. If, for example, the rate of crystallisation is lower than the rate of growth of the dissolved part of the macromolecule, then chain propagation takes place mainly at the active centres in solution and the process is described by the equation for reversible polymerisation [Eqn.(4)] with $[A]_{lim}$ corresponding to the monomer $\rightleftharpoons$ dissolved polymer equilibrium.

With decrease of the monomer concentration, the rate of growth of the dissolved part of the macromolecule becomes less than the rate of crystallisation and the kinetics are described by the same equation (4) but with another limiting monomer concentration, that in equilibrium with the crystalline polymer.

Accordingly, a number of anomalous features are observed in the polymerisation of trioxane: apparently high reaction orders with respect to the monomer and their dependence on the nature of the solvent, temperature, etc. These features cannot be explained by any ideas concerning the ionic liquid-phase processes other than those described above.

The situation where not only the initial monomer but also other "secondary" comonomers, formed via a depolymerisation mechanism, are in equilibrium with the polymer chain is fairly common. The study of a system of such equilibrium yields valuable additional information about the process. In the polymerisation of trioxane not only the initial monomer (Tr) but also formaldehyde (F) and an eight-membered cyclic acetal–tetraoxane (TTR) (larger rings are present in smaller amounts) are present in the system in equilibrium with the polymer, so that the process can be described by the following scheme:

$$\begin{array}{ccccc} & & F & & \\ & & \downarrow\uparrow & & \\ T_r & \rightleftarrows & P_d^{(\nu)} & \rightleftarrows & P_s , \\ & & \uparrow\downarrow & & \\ & & TTR & & \end{array}$$

where P_s and $P_d^{(\nu)}$ are the solid polymer and the dissolved ends of the polymer chain with a degree of polymerisation ν respectively. This scheme makes it possible to explain the dependence of the stationary formaldehyde and tetraoxane concentrations on that of trioxane and also the anomalous dependence of the rate of polymerisation and of the induction period on the initial monomer concentration[81].

†Mechanism (3) is not shown in the original Russian text (Ed.of Translation).

Another important aspect of the kinetic-thermodynamic approach to polymerisation processes is the possibility of regulating the polymer structure by carrying out the reaction in the vicinity of the thermodynamic monomer–polymer equilibrium. The essential feature of such regulation consists in the following. The differences between the chemical potentials of the states of the polymers having different structures at high monomer concentrations, i.e. under conditions remote from equilibrium, are usually significantly smaller than the change in the chemical potential in the monomer–polymer transition. Therefore, all possible structures of the polymer are thermodynamically almost equally probable and the preferential selection of structures takes place only for kinetic reasons as a function of the type of catalyst, temperature, and solvent. However, if the polymerisation is carried out under conditions close to the monomer–polymer equilibrium, then certain structures are thermodynamically prohibited, so that at low monomer concentrations small differences between the chemical potentials of the initial and final states of the polymer can be both positive and negative. In the limiting case, the polymer formed must have only the thermodynamically most favourable structure.

If one considers the supermolecular structure of the polymer, it is found that the latter varies with the ratios of the rates of three processes: the chemical formation reaction of the polymer, the segregation of the polymer as a separate phase, and structural transformations within the polymer phase. Different supermolecular structures have indeed been observed in the polymerisation of a series of monomers in different solvents with variation of the thermodynamic polymerisation conditions by varying the monomer concentration. For example, in the polymerisation of trioxane and triethylenediamine, small globular structures are formed at a high monomer concentration, while at low concentrations the products are large well-organised lamellar crystals[86–88].

V. SOLID-PHASE POLYMERISATION

The kinetics of reactions in the solid phase are significantly specific. The differences between them and those of reactions in the gas and liquid phases are related, on the one hand, to the difference between the energies of individual molecules and the appearance of collective energy levels and, on the other, to the geometrical fixation of the molecules in space relative to one another and the appearance of different types of defects in the structure of the substance.

The study of solid phase polymerisation developed extensively in the 1960s and has at present become an independent branch of polymer chemistry. The polymers formed in the solid phase differ in their chemical structure, stereoregularity, crystallinity, and orientation from the polymers synthesised by the usual methods in solutions[89]. Studies of the polymerisation of various monomers (trioxane, tetraoxane, hexamethylcyclotrisiloxane, etc.) in the solid phase under the influence of ionising radiation or ionic catalysts established[90] that the polymerisation kinetics are in many respects identical regardless of the method of initiation. This made it possible to devise a general kinetic scheme for solid phase polymerisation taking into account the characteristic features of the structure of the solid. This concept is based on the following ideas[90].

1. As a result of the virtually complete absence of the translational diffusion of polymer molecules, monomer molecules, or various impurities, the migration of the active centre in space and its collisions with the monomer or impurities take place mainly as a result of chain propagation steps.

2. The inhomogeneities in the crystal lattice (dislocations, tracks, vacancies, etc.) are the sites where the growing polymer chains are terminated.

3. The anisotropy of the reactivity of the macromolecules growing in the crystal lattice determines their preferential growth along one of the crystallographic axes.

Thus the active centres having the same chemical structure but located in different environments exhibit different reactivities. The transfer of the active centre from one environment to another takes place as a result of the chain propagation step or some kind of physical process involving a change in the structure or in the perfection of the crystal lattice[90–94].

VI. POLYMERISATION UNDER EXTREME CONDITIONS

Together with the traditional chemical methods for influencing ionic polymerisation processes, considerable possibilities are associated with physical methods. Only the influence of the temperature and medium are widely used in practice; the influence of a high pressure and an electric field have been much less investigated but are extremely promising.

1. Polymerisation Under Pressure

Although the form of the dependence of the rate constant for an elementary reaction k on the pressure p is general and is described by the formula

$$\frac{d \lg k}{dp} = -\frac{\Delta V^{\neq}}{RT},$$

where $\Delta V^{\neq}$ is the change in volume on activation, the influence of pressure on polymerisation can be extremely complex because different values of $\Delta V^{\neq}$ occur for different elementary polymerisation steps. This has been established in a comparative study of the influence of pressure on the radical polymerisation of propene and methyl methacrylate, the cationic polymerisation of styrene and tetrahydrofuran, and the solid-phase polymerisation of trioxane[95,96].

In the radical polymerisation of α-olefins the possibility of obtaining a high-molecular-weight polymer is limited by the appearance in the chain propagation reactions of the relatively inactive allyl radicals, formed as a result of chain transfer to the monomer. It has been shown[95] that the application of pressure (>3000 atm) in the polymerisation of propene imparts "life" to the allyl radicals with a significant increase of the reinitiation rate constant. The influence of pressure on the molecular weight obeys a complex relation; however the growth of $\bar{P}_n$ with pressure is highly pronounced. In the radical polymerisation of methyl methacrylate, an increase of pressure leads to an increase of both the rate of polymerisation and of the molecular weight, which is related to the increase of k_p and the decrease of the rate constant for the destruction reaction.

In the cationic polymerisation of styrene under the influence of $HClO_4$ in chlorobenzene, a significantly more appreciable accelerating influence of pressure is observed than in radical polymerisation; this difference has found a natural explanation as a result of the decrease of the dielectric constant under the influence of pressure[96].

The solid phase polymerisation of trioxane (in the presence of I_2 as the initiator at 50–70 °C) is sharply retarded with increase of pressure, which is accompanied by the anomalously high value $\Delta V^{\neq} = 120$ cm^3 mol^{-1}. In this process the polymer chain is known to grow while disrupting the crystal lattice of the monomer[90]; pressure prevents such breakdown and leads to an effective decrease of the rate of polymerisation.

Unexpected effects were obtained when a system undergoing polymerisation was subjected to the simultaneous influence of pressure and shear deformations (see Zharov's review in the present issue).

2. The Influence of the Electric Field

Ionic polymerisation systems are in essence aqueous solutions of electrolytes in which some of the ions are active centres in the growing polymer chains, i.e. are fixed on macromolecules. By applying an electric field, it is possible to displace the ion pairs $\rightleftharpoons$ free ions equilibrium towards the latter in a manner very familiar for many of the usual systems in high electric fields whose strength exceeds 50 kV cm^{-1}.

In contrast to low-molecular-weight electrolytes, the mobility of the macroion is significantly lower than that of the counterion. As a consequence of this, the application of an electric field entails the formation of a space charge in fields whose strength is ~1 kV cm^{-1} together with an increase of the degree of dissociation of the polymeric ion pairs (as a result of the preferential removal of the counterion to the electrode). A detailed theory of the transient processes occurring in polymerisation systems following the application of an external field has been developed[97–99] and a relation has been established between the parameters of the electric field and the reaction kinetics.

When both macrocations and macroion pairs with propagation rate constants k_+ and $k_\pm$ are involved in the process simultaneously, the corresponding ratio of the rate of polymerisation in the electric field (w_E) to that in its absence (w_0) is

$$\frac{w_E}{w_0} = \frac{1 + (k_\pm/k_+ - 1)\,\bar{P}_E/c_0}{1 + (k_\pm/k_+)\,\alpha} ,$$

where c_0 is the concentration of the active centres, α the degree of their dissociation, and $\bar{P}_E$ the average stationary concentration of active centres, which depends on the mobilities of the macroion and counterion, the electric field strength, and the rate constant for the discharge of the ions at the electrode. The conditions under which the rate of polymerisation should increase or the latter should be inhibited following the application of a field have been determined[97,98,100]. Together with the change in the rate of polymerisation under the influence of the electric field, the molecular weight of the polymer increases. For a specific ratio of the constants $k_\pm$ and k_+, the degree of polymerisation increases throughout the reaction volume or in separate sections of the latter[101,102]. For example, the rate of polymerisation of trioxane under the influence of $SnCl_4$ in nitrobenzene increases by a factor of 2–7 when a field is applied, while the molecular weight of the polymer doubles[102].

3. Polymerisation Near the Consolute Point

One of the first studies of polymerisation near the consolute point for a binary liquid mixture was that of the radical polymerisation of acrylonitrile in heptane in the region of the phase diagram which includes the consolute point and corresponds to the separation of the system into two phases[103]. The interest in these investigations is due to the fact that, in the vicinity of the consolute point, there is an anomalous decrease of the macroscopic diffusion coefficient, an enhancement of the concentration fluctuations, an increase of the viscosity of the system, etc. It is to be expected that the anomaly in the physical properties of the medium has an unusual effect on the polymerisation reaction. Indeed, in the polymerisation of acrylontrile in the vicinity of the consolute point, distinct minima are observed in both the rate of polymerisation and in the molecular weight of the polymer. Kinetic studies combined with the investigation of the state of the system near the consolute point by the paramagnetic label method suggest that the polymeric radicals can give rise to stable clusters[103–105]. Similar phenomena apparently play a significant role in certain multiphase systems.

VII. INTERCHAIN EXCHANGE IN POLYMERS

In 1962 Enikolopov[106] pointed out the possibility of interchain exchange in polymerisation reactions and proposed a mechanism for this reaction, which was subsequently called the reaction involving chain transfer via the polymer with the dissociation of the macromolecule (CTD).[107–110]

The interchain exchange reactions in polycondensation processes had been well known long before the studies of Flory and Korshak were undertaken[111–114]. However, it was believed that interchain exchange is possible only in polycondensation processes and it was regarded as one of the fundamental differences between polycondensation and polymerisation processes. It is nowadays generally recognised that the capacity for interchain exchange is determined solely by the structure of the macromolecule and the type of the active centre and is characteristic of all heterochain polymers regardless of the method of their synthesis.

The essential feature of the CTD reaction is the exchange interaction of two chains, one of which constitutes the active centre and the other an inactive macromolecule, which proceed via a heterolytic or homolytic substitution mechanism. In a general form, the mechanism of the CTD reaction can be represented schematically as follows:

$$\sim(R^1)^{\bullet} + X \rightleftarrows \sim R^1{-}\overset{R^2}{\underset{R^3}{X^{\bullet}}}{-} \begin{cases} \rightleftarrows \sim(R^2)^{\bullet} + \sim R^1XR^3\sim \\ \rightleftarrows \sim(R^3)^{\bullet} + \sim R^1XR^2\sim \end{cases} \quad (5)$$

where X is a heteroatom (O, N, S, P, Si, etc.) and $\sim(R^i)^*$ an active macrospecies (cation, anion, or radical).

The above mechanism is fairly universal and makes it possible to understand the fundamental kinetic features of the ionic polymerisation reactions of heterocycles and also the form of the variation of the molecular weight distribution of the macromolecules in these processes.

The CTD reaction is in essence yet another stage (together with chain initiation, propagation, and transfer reactions) in the formation reactions of macromolecules.

1. The CTD Reaction as a Factor Governing the Attainment of the Equilibrium Distribution of Macromolecules

It is seen from Scheme (5) that a process occurring via the mechanism indicated is reversible and should lead to a redistribution of the macromolecules with respect to size and composition, i.e. should influence important properties of the

polymers formed, such as the MWD and the distribution of units in the copolymers, which determine in their turn the fundamental physicomechanical and rheological characteristics of the polymers. Evidently[74,115,116] an equilibrium characterised by the most probable distribution of macromolecules with respect to size must be ultimately established in the system where the CTD reaction takes place; here one must note particularly that this distribution is established regardless of the details of the mechanism and the rates of any other reactions occurring in the system. For linear molecules, the equilibrium MWD function is

$$\frac{[R_j]}{\sum_{i=1} [R_i]} = \frac{1}{P_n} \exp(-j/P_n), \qquad (6)$$

where $[R_j]$ is the concentration of macromolecules with a length j and P_n is the number-average degree of polymerisation.

It is noteworthy that the above MWD function is used only for the description of macromolecules with flexible chains; for macromolecules with rigid chains, the MWD function becomes narrower and, for example, for rigid rods, assumes the form[107,117]

$$[R_j] \propto j^2 \exp(-3j/P_n).$$

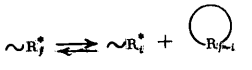
The form of the equilibrium distribution function is also determined by the interaction of the macromolecules with the medium: in a θ-solvent, in moderately concentrated solutions, and in bulk, Eqn.(6) is valid, while in the case of a dilute solution in a good solvent the exponential distribution assumes a different form[110,116]:

$$[R_j] \propto \exp\left(\frac{5}{2}\alpha^2 + \ln \alpha^3 - \gamma j\right),$$

where γ is a constant coefficient and α the degree of swelling of the macromolecule in solution, which depends on its length (i.e. on j).

If the polycondensation or polymerisation reaction takes place in a poor solvent, from which the polymer is precipitated to form a separate phase, then the equilibrium MWD is also exponential. A detailed thermodynamic analysis of such systems has been carried out[116].

It follows from Scheme (5) that the object of attack by the active centre of the macromolecule can also be its own chain. Evidently, under these conditions cyclic macromolecules with different molecular weights are formed together with linear macromolecules. This situation is fairly characteristic and in many polycondensation (the formation of polysiloxanes, polyesters, polyamides, etc.) and polymerisation (the synthesis of polyacetals, polyesters, polyethers, polyamides, etc.) processes the formation of both low- and high-molecular-weight cyclic products is observed[107,110-113]. In this case the CTD reaction can be represented schematically as follows:



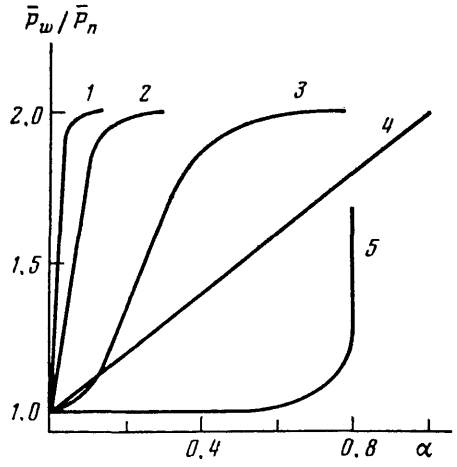
Apart from monocyclic species, in concentrated solutions of polymers with flexible chains there is a possibility of the formation of catenanes and in the case of polyfunctional polymers rings with a very complex topology can be produced[118] (pp.133–139).

The equilibrium distribution of rings with respect to size has been obtained on the freely jointed chain model[119]:

$$[R_j] \sim j^{-5/2} \exp(-j/P_n). \qquad (7)$$

This equation is valid only for the description of MWD of fairly large rings; on the other hand, in the case of small and moderately large rings (up to 10–12 members) their energy strain plays an important role and Eqn.(7) therefore becomes unsuitable.

We considered above the MWD functions at equilibrium, which can be established in a macromolecular system not only via the mechanism of a CTD reaction but also as a result of polycondensation or reversible polymerisation. The fundamental difference between these mechanisms of the formation of a polymer with an equilibrium MWD consists in the kinetics of its attainment[107,120-123], which is illustrated in the Figure. In polycondensation, the parameter $\bar{P}_w/\bar{P}_n$, characterising the width of the distribution, increases linearly with the degree of conversion (see Figure, curve *4*). In reversible polymerisation a narrow MWD ($\bar{P}_w/\bar{P}_n = 1$) is maintained virtually until the attainment of the equilibrium degree of conversion and $\bar{P}_w/\bar{P}_n \to 2$ only within a very short range of degrees of conversion following the attainment of equilibrium (curve *5*). In contrast to the previous instances, the rate of establishment of the equilibrium MWD in a CTD reaction depends on the chain length and increases sharply with increase of the latter (curves *1*–*3*) owing to the increase of the number of reaction centres.



The character of the variation of the width of the distribution ($\bar{P}_w/\bar{P}_n$) in polymerisation and polycondensation processes[107]: *1*)–*3*) polymerisation without chain termination and with instantaneous initiation in the presence of CTD [$k_{CTD}/k_p = 1$; monomer/catalyst concentration ratio: *1*) 10^4; *2*) 10^3; *3*) 10^2]; *4*) linear polycondensation in the absence of CTD; *5*) reversible polymerisation without chain termination and chain transfer; α = degree of conversion.

The results of the analysis of the kinetics of the attainment of the equilibrium MWD, presented in a general form in the Figure, show that the CTD reaction is a much more vigorous process, leading to the attainment of the equilibrium MWD, than polycondensation or reversible polymerisation. The character of the $\bar{P}_w/\bar{P}_n$–α kinetic curves is a criterion of the occurrence of the CTD reaction in the reaction system and is used for a quantitative assessment of the relative rate of this reaction ($\varepsilon = k_{CTD}/k_p$, where k_{CTD} is the rate constant for the CTD reaction and k_p the chain propagation rate constant). In particular, such estimates have been carried out for polyacetals[122] and polyethers[123].

When copolymer formation reactions are considered, the question of the kinetics of the attainment not only of the equilibrium MWD but also of the equilibrium distribution of the macromolecules with respect to composition and of the distribution of units in the chain arises.

It has been shown theoretically that the distribution of the sequences of units of each type with respect to length in the copolymer obeys an exponential law[107] and the average number of blocks in the chain (l) is described by the expression[124]

$$l^2 = K(m_a - l)(m_b - l) ,$$

where K is a combination of the rate constants for the cross-exchange reactions between the chains, l the number of blocks of units of a given type in the chain, and m_a and m_b are the total numbers of monomeric units of types A and B respectively.

The relations obtained have been confirmed experimentally for a series of objects in a number of investigations[11,36,40,46,125–131]. It is noteworthy that in the general case the quantitative study of the formation of polymers in the interaction of two homopolymers or the study of the polymerisation of one of the monomers in the presence of another homopolymer is extremely difficult and this problem has been solved successfully only in the study of thermostable formaldehyde copolymers[127,129]. However, the problem simplifies considerably if one employs model low-molecular-weight compounds. In this case it is possible not only to estimate the combinations of the constants for the cross-exchange between the chains but also to determine separately all the rate constants for the elementary reactions[11,126,128,131].

2. The Role of CTD in Individual Stages of the Polymerisation Process

A second important aspect arising when the formation reactions of heterochain polymers are considered is the need to allow for the active role played by the resulting macromolecules themselves. Indeed, it is seen from Scheme 5 that the CTD reaction proceeds via an intermediate stage involving the formation of an unstrained 'onium ion whose reactivity differs in the general case from that of the growing active centre. As a consequence of this, the nature and concentration of the active centres change. The kinetic effects are then in essence caused by the competition between the chain propagation reactions at the free active centres (R_j^*) and the active centres bound in a complex with a macromolecule $(R_jp)^*$. These reactions can be represented by the following kinetic scheme:

$$R_j^* + m \xrightarrow{k_1} R_{j+1}^* ,$$

$$R_j^* + p \rightleftarrows (R_jp)^* ,$$

$$(R_jp)^* + m \xrightarrow{k_2} R_{j+1}^* + p .$$

Evidently, the case where $k_2 < k_1$ corresponds to the progressive retardation of the chain propagation reaction. If $k_2 = 0$ and the equilibrium in the complex formation reaction between the growing active centre and the macromolecule is strongly displaced to the right, the implication is that the growing active centres are deactivated in the given system and that the rate of polymerisation decreases until the complete arrest of the reaction. It has been shown in a series of experimental studies that both these cases are characteristic of the ionic polymerisation of heterocycles[14,22,35,132,133]. Thus in the cases considered, the influence of the macromolecules formed reduces mainly to the inhibition of the polymerisation process.

The macromolecules are actively involved also in the initiation stage[107], because the growing active centres can be formed in the interaction of the catalyst (Ct) with both the monomer and the polymer:

$$Ct + m \xrightarrow{k_1} R_1^* ,$$

$$Ct + p_j \xrightarrow{k_2} R_i^* + p_{j-i} .$$

Under the influence of the catalyst, the macromolecules decompose under these conditions to yield growing active centres, which do not differ in their chemical nature from those arising on direct interaction of the catalyst with the monomer. When $k_2 > k_1$, the rate of accumulation of the active centres in the polymerisation system increases progressively, so that the polymerisation should be clearly autocatalytic. A whole series of similar instances have been observed experimentally in the cationic polymerisation of cyclic acetals under the influence of protic and aprotic acids[29,36,134].

The second possible version of the involvement of macromolecules in the initiation step corresponds to the scheme

$$Ct + m \xrightarrow{k_1} R_1^* ,$$

$$Ct + p_j \rightleftarrows Ct p_j .$$

In this case, the macromolecule reacts with the catalyst molecules to form complexes which are inactive in polymerisation, playing the role of a kind of inhibitor. The fraction of the catalyst bound in a complex with the polymer is determined by the relative basicities of the heteroatom in the monomer and polymer molecules. Such a situation frequently arises in the polymerisation of many cyclic ethers under the influence of Lewis acids[135,136].

If a low-molecular-weight substance is present in the polymerisation system and is involved in the reaction as a chain transfer agent, then the reaction

$$R_j^* + XY \xrightarrow{k_n} R_jY + X^*$$

results in the formation of an active fragment X* whose reactivity towards the monomer is in general different from that of the growing active centre. The reinitiation reaction can occur when the active fragment X* interacts with the monomer or polymer molecule:

$$X^* + m \xrightarrow{k_1} R_1^* ,$$

$$X^* + p_j \xrightarrow{k_2} R_i^* + p_{j-i} .$$

If the case where $k_1 \ll k_p$ and $k_2 \gg k_1$ obtains, then analysis shows[107] that a completely unusual autocatalytic character of the polymerisation process itself and the consumption of the chain transfer agent should be observed. Such a case has in fact been noted in the polymerisation of dioxolan in the presence of chain transfer agents generating a proton as the active fragment[137].

The different versions examined demonstrate convincingly that one cannot understand the extremely complex kinetics of the ionic polymerisation of heterocycles without taking into account the active role which the macromolecules formed themselves play in such polymerisation. The macromolecules influence all the stages of the polymerisation process—the initiation of the growing centres and the propagation, transfer, and termination of the reaction chains. This influence is exerted because each active species in the system is capable of reacting with any unit of the polymer chain to form an active centre bound in a complex, whose decomposition results in the formation of new active centres with a modified reactivity.

This is manifested particularly strikingly in the copolymerisation of heterocycles when the interchain exchange processes occurring in the system supplement the cross-exchange reactions, which leads to an alteration of the concentrations of all types of growing active centres. In consequence of this, the dependence of the composition of the copolymer formed on that of the monomer mixture is not described by the classical Mayo-Lewis equation. This problem has been analysed in detail and methods have been developed for the determination of the copolymerisation constants in the presence of the CTD reaction[107,126]. The use of the classical version of the Mayo–Lewis equation leads to effective copolymerisation constants which must be approached with much caution.

It remains to note yet another important feature of systems in which the CTD reaction occurs, namely the appearance of a special kind of "living" state of the polymerisation system[107, 109,114,138]. It is characterised by the fact that, in contrast to the classical "living" polymerisation[1], in the CTD reaction each "dead" macromolecule can be "revived" regardless of the nature of the terminal groups. This ultimately results in the involvement of all the macromolecules, both "living" and "dead", in the propagation process.

One of the important aspects of the relevant studies is investigation of the detailed mechanism of the elementary step in the CTD reaction. In a general form, it can be represented by Scheme (5), but in each specific instance, when the chemical nature of the polymer chain is varied, the actual reaction mechanism becomes more complex. Nevertheless, in all the instances investigated, it has been shown that the reaction must proceed via the intermediate formation of an active growing centre bound in a complex with a macromolecule[40,107,120,132]. For example, it has been shown[132] that the interaction of the macrocation with the chain leads to a large increase of viscosity owing to the effective increase of the molecular weight.

The exchange reactions can be simply and conveniently modelled with the aid of low-molecular-weight compounds, which simulate particular functional groups involved in the CTD. The low-molecular-weight compounds model either the reagent (the growing active centre) and the substrate (the macromolecule attacked by the active centre) or only the substrate. In the latter case only the chain transfer to the low-molecular-weight compound is in essence investigated. Such studies have been carried out for a whole series of compounds: ethers[120], esters[40,46,125,139–142], and acetals[4,11, 36,106,143]. The available information about the mechanisms of many interchain exchange reactions in various derivatives of carboxylic acids, sulphur-, phosphorus-, silicon-, and metal-containing compounds, and certain other systems has been surveyed and described systematically in a monograph[107].

3. CTD As a Method of Synthesis

The possibility of the practical employment of interchain exchange reactions for the synthesis and chemical modification of polymeric materials is very important. Their use for the synthesis of statistical block and graft copolymers as well as polymers with specified terminal functional groups is most promising. In principle, there is a possibility of two methods of synthesis of copolymers using interchain exchange reactions: the polymerisation of the monomer in the presence of another homopolymer and the interaction of two homopolymers.

In the former case, i.e. in the polymerisation of the monomer in the presence of another homopolymer, the polymerisation is accompanied by CTD to the "foreign" homopolymer present in the system. At the beginning of the process, a block copolymer is formed and then transformed into a statistical copolymer as the vigorous interchain exchange reaction proceeds. This method has been applied to a number of systems, in particular to the cationic polymerisation of cyclic ethers, esters, and acetals in the presence of heterochain polymers of different kinds[130,139,144].

If the comonomers differ sharply in their reactivities, then their copolymerisation leads initially to the homopolymerisation of the more reactive monomer and then the less reactive monomer polymerises in the presence of the second homopolymer. In the absence of interchain exchange such a reaction would have led to the formation of a mixture of homopolymers but in systems where a sufficiently intense interchain exchange takes place a statistical copolymer is produced. The copolymerisation of trioxane with dioxolan, where the latter is consumed during the induction period of the polymerisation of trioxane, proceeds in this particular way[145]. A similar situation obtains also in a number of other systems[107].

In such cases one should speak of polymerisation in the presence of another homopolymer rather than copolymerisation, although externally the process appears to be the usual copolymerisation. On this basis, a method has been developed for the synthesis of mixed carboheterochain block copolymers[146], which is the most general of those known at the present time[107]. It consists in the cationic or anionic polymerisation of vinyl monomers in the presence of heterochain polymers, whose bonds may be ruptured under the influence of the growing ions. This method is entirely universal; any heterochain polymers obtained by both polymerisation and polycondensation can be used in the reactions and the reaction itself can be carried out both homogeneously and heterogeneously. It is important that the polymerisation process can also be carried out directly on the finished articles (fibres, films) made of heterochain polymers, which makes it possible to modify the properties of only a thin surface layer.

When two homopolymers interact in the presence of a catalyst, block or statistical copolymers are also produced[107].

If the heterochain homopolymer is made to react with low-molecular-weight compounds, which behave as agents transferring the reaction chain, then the polymer is degraded and the chains formed contain the corresponding terminal groups. This principle has been used to obtain polymers and oligomers with specified end groups and it can be applied also in the usual version of the polymerisation of a monomer in the presence of a chain-transfer agent[107]. When the interchain exchange reactions take place in such systems, the relative rates of consumption of the reactants (of the monomer and the chain-transfer agent) are unimportant for the final result, since a continuous redistribution of the end groups in the macromolecule takes place under these conditions.

The above methods for the modification of heterochain polymers have been used successfully for the solution of various practical problems and in the first place for the thermal stabilisation of polymers based on formaldehyde. Above the limiting temperature, such polymers decompose fully to the monomer as a result of depolymerisation. This virtually precludes their conversion into finished articles, since the temperature at which this is done usually exceeds the limiting temperature. This contradiction can be resolved by creating conditions under which the induction period of the given chain process is significantly longer than the time necessary for the working of the polymer. Depending on the degradation mechanism[110], this can be achieved in two ways. If the initiation reaction of the thermal degradation of the polymers begins from the end of the chain, then end groups whose thermal decomposition takes place above the limiting temperature for the given polymer must be introduced

into the latter. On the other hand, if the initiation is random, as, for example, in the thermo-oxidative degradation of polyformaldehyde, then the introduction of stable units by the formation of a copolymer makes the kinetic chain length in the degradation process significantly smaller than the average chain length of the copolymer.

Both these procedures have been applied successfully using the interchain exchange reaction for the solution of the problem of the thermal stabilisation of polymers based on formaldehyde. The following methods have been developed for the synthesis of formaldehyde homopolymers and block copolymers via a cationic mechanism (using catalysts of the type of Lewis acids and their complexes): (a) polymerisation with stabilisation of the end groups via chain transfer to low-molecular-weight linear acetals[147,148]; (b) copolymerisation of formaldehyde with cyclic acetals[149, 150]; (c) polymerisation of formaldehyde accompanied by chain transfer with dissociation of macromolecules into polymeric acetals or ethers[127,151,152]; (d) exchange reactions between polyformaldehyde and linear polyethers and polyacetals[153].

The study of copolymerisation by the second of the methods listed above in the gas phase in a flow system showed that a special type of copolymerisation takes place in which a true copolymer is obtained despite the fact that the monomers are polymerised on active centres of different types[149].

Oligomeric products of different types with two functional reactive groups, obtained using the interchain exchange reaction, found extensive applications as starting materials for the synthesis of polymers, plasticisers, intermediates in organic synthesis, surfactants, etc.[107,120,154]

One of the exceptionally important problems in practice is the employment as a secondary starting material of used articles made of polymeric materials or of industrial waste. In the case of polymers having heterocarbon linkages in the main or side chains, the application of the interchain exchange reactions to the solution of this problem is of interest. A series of successful examples of this kind already exist[107,155], but the extensive possibilities inherent in the interchain exchange reaction for such purposes have still been inadequately employed in theoretical research and in practice.

This review has dealt with the results of kinetic and structural studies of cationic polymerisation reactions of heterocycles. The set of data obtained for the mechanisms of the reactions investigated demonstrate convincingly the fruitfulness of the kinetic approach. Further development of this field will be directed towards the determination of quantitative kinetic data; this will make it possible to develop and supplement the existing ideas concerning the nature of the active centre in the cationic polymerisation of heterocycles and to establish a relation between its reactivity and structure.

An important kinetic method involves the study of low-molecular-weight models. In this case it is frequently possible to obtain the most clear-cut correlations between the kinetic constants and thermodynamic parameters, i.e. the structure of the reacting substances. However, the complete transfer of the results obtained to polymeric objects is not always possible, since the polymeric nature and the specific features of the physical state of the polymer chain are in many instances largely manifested in the chemical reactions of the polymers; an example of this is provided by zwitter-ions. Allowance for the physical state of the system in the study of the kinetics of the formation reactions and transformations of macromolecules becomes more important the finer the details of the mechanism in which the investigator is interested.

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