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Recent trends in research into ionic polymerisation

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ABSTRACT. The results of original studies on the mechanism of formation of macromolecules in ionic systems are discussed. Amongst these are polmerisation involving living carbocation chains, cationic processes that occur via the activation of a monomer, anionic polymerisation initiated by aluminium and zinc porphyrins, group transfer polymerisation, and polymerisation of olefins using homogeneous Ziegler–Natta catalysts that exhibit high activity.

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I. Introduction

During the last ten years the range of agents capable of initiating the ionic polymerisation of various monomers has increased considerably. Many agents have been successfully used to solve important practical problems, such as the preparation of novel polymers, simplifying the conditions for the synthesis of narrowly dispersed macromolecules, and the development of highly effective polymerisation processes. The properties identified in original initating systems have had a marked influence on existing ideas about the mechanism of formation of macromolecules in ionic processes. In the present article particular attention is given to this very question. The desirability of discussing it arises from the fact that the trends in research which will be considered below have so far not been reflected in the Russian review literature.

We should mention that in comparing cationic with anionic polymerisation it was customary to emphasise the marked difference in stability of the active sites. The specific features of polymerisation occurring via active anionic sites are as follows: a linear increase in molecular weight (MW) of the polymers with conversion, and a narrow molecular weight distribution (MWD). These characteristics, which had been established for a number of specific processes, were for a long time considered unattainable for active cationic sites.

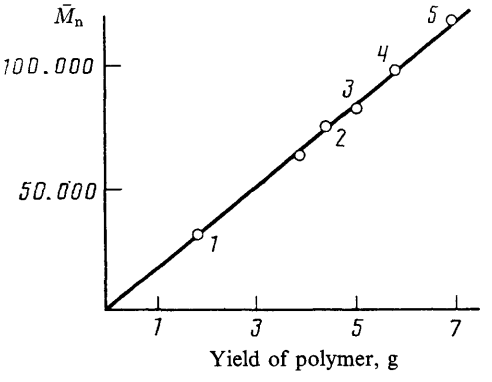


Figure 1. Polymerisation of isobutylene by the system dimethoxy-*p*-dicumyl (DMDC)–$TiCl_4$ in the mixed solvent $CH_3Cl-C_6H_{14}$ (40:60 by volume) at −80 °C.[9] Concentration, mol litre^{-1}: $TiCl_4$ 1×10^{-3}, DMDC 6.4×10^{-5}; total volume 25 ml; conversion 100%; values of $\overline{M}_w/\overline{M}_n$: *1*, 1.11; *2*, 1.10; *3*, 1.17; *4*, 1.10; *5*, 1.09.

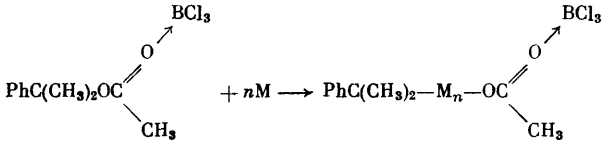
II. Cationic processes

1. Mechanisms of cationic processes

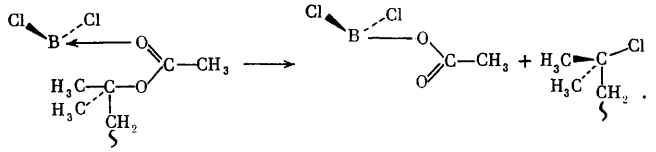
A comparison of the practical significance of the results that characterise cationic and anionic polymerisation has often pointed to the considerable advantage of the latter. This has mainly been connected with the possibility of synthesising various block and multiblock copolymers with a widely controlled range of physicomechanical properties in anionic rather than cationic systems. The development of novel cationic initiators has substantially altered this situation in recent years, and this contrasting position has now lost its original importance.

Studies undertaken in recent years led to a revision of this idea. The basis for this was provided by the studies by Kennedy et al. that developed from previous research by the same authors which focused on the so-called "quasi-living" chains. The results of these studies were examined in a previous review.[1] We shall confine ourselves to the following observation: the distinctive features of polymerisation processes involving quasi-living chains are governed by slow batching of the monomer into the reaction mixture ($3-5 \times 10^{-3}$ mol min^{-1}); this technique results in a marked narrowing of the molecular weight distribution compared to polymerisation under normal conditions. For example, in the case of *p*-t-butylstyrene with the use of boron chloride–cumyl chloride as initiating system in dichloromethane at −50 °C and a conversion of 100%, the $\overline{M}_w/\overline{M}_n$ ratios were 6.53 and 1.38 respectively for introduction of monomer in a single batch and gradually.

The characteristics of the growth of living chains were identified when initiating systems containing Lewis acids in combination with cumyl ethers or esters were used.[2–25] Boron chloride and cumyl acetate (CA) or methyl cumyl ether were used most frequently as components of these systems. For this type of polymerisation the formation of polymers with $\overline{M}_w/\overline{M}_n$ almost equal to 1.1 is typical as is a retention of the linear dependence of $\overline{M}_n$ on the degree of conversion up to 100%. This is shown in Fig. 1 in the case of the polymerisation of isobutylene. The following scheme[4] illustrates the mechanism for polymerisation of this monomer (M) with the system boron chloride–CA

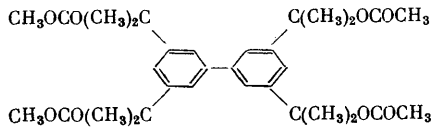


Deactivation of the living polymers, which is caused in particular by an increase in temperature of the reaction mixture, results in the formation of macromolecules with a terminal chlorine atom, which has been interpreted in the following way:[2]



It is worth noting that terminal chlorine atoms have also been found in polymers deactivated by nucleophilic reagents; no details about the mechanism of this effect were given by Faust and Kennedy.[2]

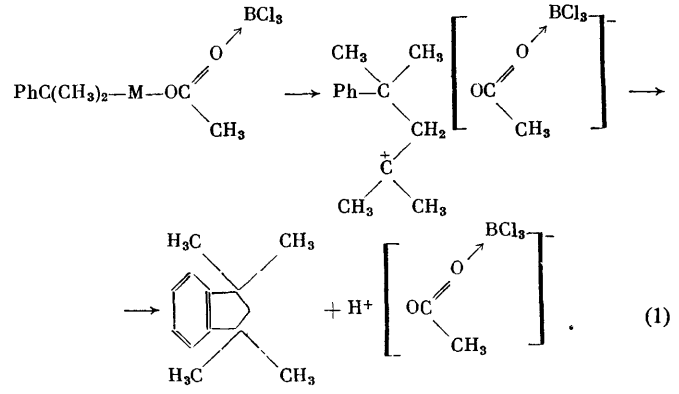
Interesting results are obtained by replacing CA and methyl cumyl ether with the di-, tri- and tetra-functional analogues of these compounds.[4,6–8,11] The last of these has the structure (I):



(I)

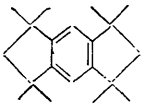
"Tetrablock" macromolecules were obtained from this compound. Polymerisation in the system isobutylene–(I)–BCl_3–CH_2Cl_2 at –80 °C gave this result.[11]

The above processes are accompanied by side reactions that result in the formation of indane rings. This is typical for growing cationic chains containing aromatic rings. Such cases are illustrated by the following scheme:[6]



(1)

For bifunctional initiators the formation of diindane structures is possible:



The relative role of these reactions depends on the temperature and nature of the medium. A reduction in the polarity of the solvent and temperature may lead to their being completely excluded, as depicted in Fig. 2.

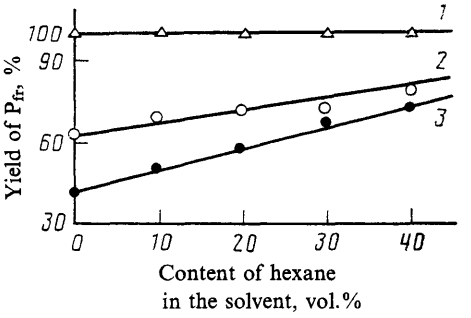


Figure 2. Effect of polarity of the medium and temperature on the formation of polyisobutylene free of indanyl groups (P_{fr}).[6] Initiating system BCl_3–DMDC; temperature, °C: *1*, –70; *2*, –50; *3*, –30.

Let us consider the preferred use of boron chloride compared to other Lewis acids in initiating systems by the authors of these studies. This also refers to the above-mentioned polymerisation processes involving quasi-living chains.[1]

The characteristics of boron chloride are revealed when it is compared with certain aluminium derivatives that form highly active initiating systems with the compounds R_3CCl or HCl. The former do not yield any suitable initiators with BCl_3 while the combination of BCl_3 and HCl constitutes an equilibrium system with a low initiating activity. According to Kennedy and Chen,[12] the reason for this is the low stability of the BCl_4^- counterion, which undergoes reaction (2*c*):

$$HCl \cdot BCl_3 \underset{a}{\rightleftarrows} H^+, BCl_4^- \xrightarrow[b]{(CH_3)_2C=CH_2} (CH_3)_3\overset{+}{C}, BCl_4^- \xrightarrow{c} \longrightarrow (CH_3)_3CCl + BCl_3. \quad (2)$$

The features that are typical of living carbocation chains are also found in the polymerisation of styrene monomers. In this respect the best results have been obtained for 2,4,6-trimethylstyrene,[10] whose structure excludes side reactions of the type (1).

In some studies titanium tetrachloride has been used as a component of the initiating systems. A combination of it and *p*-dimethylcumyl ether (DCE) proved active towards isobutylene

down to −80 °C.[9] The introduction of $TiCl_4$ into a reaction mixture containing all the remaining components achieves good results ($\bar{M}_w/\bar{M}_n$ = 1.1, $\bar{M}_n \sim 10^5$). The use of a previously prepared complex of $TiCl_4$ and DCE gives rise to the formation of indane rings on one or on both ends of the chain. This effect led the authors to make the following assumptions.

When the initial complex is allowed to stand, it gives rise to the formation of the ion pair $\gtrless C^+ [OTiCl_4]^-$, for which an intramolecular conversion to $H^+ [OTiCl_4]^-$ is possible, accompanied by the development of an indane ring at the end of the chain. The contribution of such a conversion must depend on the length of time of storing the initial complex until its introduction into the solution of monomer, which is what actually occurs. With an increase in time for allowing the complex to stand, the content of indane rings in the polymers increases (for example, in one study[9] data is given for times of 30, 75, and 90 s). The relatively slow ionisation of the complex may be attributed to the low polarity of the solvent—a mixture of methyl chloride and n-hexane in the ratio 2:3 was used.

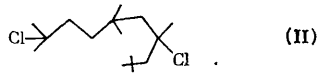
We should mention a further route for the exclusion of side reactions of the type (1) as described by Biswas and Kennedy.[3] In this case the ability of boron chloride to interact with 2,5-dichloro-2,5-dimethylhexane (DDH) was established, leading to the formation of an active initiator for the polymerisation of isobutylene. The absence of a similar effect in the case of monohaloalkanes led the authors to conclude that the bifunctionality of DDH has a special role, making it possible for a cyclic halonium ion to be formed:

$$Cl{-}C(CH_3)_2CH_2CH_2C(CH_3)_2{-}Cl \xrightleftharpoons{BCl_3} (CH_3)_2C\begin{array}{c}CH_2{-}CH_2\\ | \quad\quad |\\ \quad C(CH_3)_2\\ \quad\quad \overset{+}{Cl},\ BCl_4^-\end{array} . \qquad (3)$$

The propagating chains formed by the action of this sytem undergo spontaneous termination by the normal route (4), but the characteristic signs of reinitiation could not be detected

$$\begin{array}{c}\diagdown\\ -C^+,\ BCl_4^- \\ \diagup\end{array} \longrightarrow \begin{array}{c}\diagdown\\ -C-Cl + BCl_3. \\ \diagup\end{array} \qquad (4)$$

The combination of spontaneous termination and lack of reinitiation is indirect confirmation of mechanism (3). Positive evidence for it is also provided by the formation of the dihalide (II) on reaction of 2,2,4-trimethyl-1-pentene (TMP) with DDH and BCl_3 in CH_2Cl_2 at −20 °C, namely, with conditions under which TMP does not polymerise. For the sake of brevity, we shall use the skeletal structural depicted by Biswas and Kennedy,[3]



(II)

It follows from the above that replacement of cumyl chloride as a component of the initiating systems by cumyl ethers gives rise to a change in behaviour of quasi-living and living chains in the majority of cases. Similar qualitative effects were subsequently obtained when another method was used, namely, the addition of a catalytic quantity of a strong electron donor (ED) to binary systems of the type Lewis acid—t-alkyl chloride. The result of such an addition are illustrated by data on the polymerisation of isobutylene in a mixed solvent of n-hexane—methyl chloride (3:2) at −40 °C on treatment with the system 2-chloro-2,4,4-trimethylpentane—$TiCl_4$ in the absence and in the presence of an ED:[5]

Polymerisation conditions	$\bar{M}_w/\bar{M}_n$ of polymer
In the absence of an ED	1.21
In the presence of dimethyl sulphoxide	1.05.

In this case 2,5-di-t-butylpyridine, which acts as a proton trap but which is inert towards carbocations, was also included amongst the components of the reaction mixture. Its presence leads to removal of the proton component of the initiation reaction, which results from an uncontrolled number of proton donors. (For further details, see the review of Erusalimskii).[1] Dimethylacetamide was used as an ED in other systems of a similar type.

These compounds may be regarded as agents stabilising the active cationic sites. The hypothetical structure (III), relating to a system based on boron chloride,[4] has been put forward to explain this theory:

$$\sim\overset{\delta+}{\underset{CH_3}{\overset{|}{C}}}{-}Cl\cdots ED\cdot n\,BCl_3\cdots\overset{\delta-}{BCl_4} . \qquad (III)$$

Evidence for polymerisation occurring on living chains was found by Kennedy et al. in the case of certain chlorine-substituted styrene monomers.[3,4] In particular, in the system *p*-chlorostyrene—$TiCl_4$—2-chloro-2,4,4-trimethylpentane—methyl chloride—cyclohexane—dimethylacetamide—di-t-butylpyridine, polymerisation at −80 °C is characterised by a linear dependence of $\bar{M}_n$ on the degree of conversion.[13] However, $\bar{M}_w/\bar{M}_n$ in this case is not less than 1.26, which may be due to side reactions.

Results of practical significance were obtained by polymerisation of *p*-chlorostyrene via mono-, di-, and tri-functional living polyisobutylene chains.[14] In this way linear and three-arm block copolymers containing comparable proportions of blocks of both types were synthesised with a total value of $\bar{M}_n$ of the order of 5×10^4. Their properties are typical of thermoplastic elastomers—polymers with rubber-like and "glass-like" sequences. They have a considerable advantage over block copolymers based on butadiene and styrene that are similar in general type, but they differ from them by virtue of their increased stability towards atmospheric oxygen and lower combustibility (due to their chlorine content) while having similar physicomechanical parameters.

An assessment of the degree of success obtained from the studies carried out in this area has been given in a general summary by Kennedy,[15] in which considerable attention is given to the applied aspects.

Before the series of studies by Kennedy was published, only the polymerisation of vinyl ethers by the initiating system $HI-I_2$ could be classed as a cationic process occurring via living chains. The first studies in this area, which were carried out by Higashimura et al., have been discussed in an earlier review.[1] Let us consider more recent studies by these same authors, which extended the range of systems of a similar type and their applicability to other monomers.

A number of novel systems based on HI were obtained when I_2 was replaced by different zinc halides.[16] Their effect in relation to the polymerisation of vinyl isobutyl ether (VIBE) is briefly illustrated

by the results obtained in toluene at 0 °C and with complete conversion of monomer at concentrations (mol litre^{-1}) of: 0.38 (VIBE), 5×10^{-3} (HI), and 1×10^{-4} (ZnX_2):

X	I	Br	Cl
$\bar{M}_w/\bar{M}_n$	1.05	1.04	1.05 .

The introduction of a second equal portion of monomer after polymerisation of the first portion was complete led to the formation of polymers with $\overline{M}_n$ of the order of 1.5×10^4 while preserving a linear dependence of this value on conversion and with only a slight broadening of the molecular weight distribution ($\overline{M}_w/\overline{M}_n$ 1.07–1.08).

The possibility of replacing both the iodine components by others was demonstrated in the case of the polymerisation of VIBE in toluene by the system $(CH_3)_3SiI-ZnI_2$. Effects that were typical of polymerisation via living chains were found at −40 °C.[17] The dependence of the final result on temperature, with complete conversion of monomer and concentrations of VIBE, trimethyliodosilane, and zine iodide equal to 0.38, 0.005, and 0.001 mol litre^{-1} respectively was as follows:

t, °C	−40	0	25
M_n	8200	640	470
$\bar{M}_w/\bar{M}_n$	1.06	1.14	1.26 .

The active sites that are effective in $HI-ZnX_2$ systems have been attributed a structure containing the fragment $(I\cdots I_2)^-$ proposed for the active sites formed by interaction of monomer with a combination of HI ands I_2.[1] Generation of active sites in the last of the above-mentioned systems may be viewed in a similar manner — activation by ZnI_2 of the C–I bond in the adduct between the silane component and monomer.

The polymerisation processes of VIBE initiated by the system $HI-ZnI_2$ have been studied in the greatest detail. Of the other properties, the lifetime of the growing chain in relation to the conditions selected has been determined. We shall list the results obtained with VIBE, HI, and ZnI_2 concentrations of 0.38, 0.01, and 0.0001 mol litre^{-1} respectively:[18]

Solvent	t, °C	half-life* of active sites, min
Dichloromethane	−15	270
Toluene	−15	390
Toluene	0	180
Toluene	25	30

*The period of time over which the concentration of the active sites is halved through deactivation reactions.

The use of different iodine-containing initiating systems for the polymerisation of vinyl ethers with polar substituents [$CH_2=CHO(CH_2)_2Cl$, $CH_2=CHO(CH_2)_2CH(COOC_2H_5)_2$, $CH_2=CHO(CH_2)_2OC_6H_4X$, where X = OCH_3 or Cl] gave narrowly dispersed polymers.[19–21] Some of these were used for the synthesis of block oligomers with a given sequence of monochain residues corresponding to different monomers. An interesting example of this type is the heterotetramer obtained in toluene at −40 °C using the system $HI-ZnI_2$:[22]

$$CH_3CH(O-n\text{-}Bu)-CH_2CH[OCH_2CH_2CH(COOEt)_2]-CH_2CH\cdot$$
$$\cdot(OCH_2CH_2OCOPh)-CH_2CH[OCH_2CH_2OCOC(CH_3)=CH_2]OCH_3.$$

It is formed as a result of the activation of the adduct of vinyl n-butyl ether and hydrogen iodide by zinc iodide and the step-wise introduction of equimolar quantities of the other three monomers into the reaction mixture. By using 2-(vinyloxy)ethyl methacrylate as one of these (the last one in this case) this tetramer may be considered capable of undergoing addition polymerisation.

Table 1. Synthesis of block copolymers through living polymers corresponding to monomer M_1.[23]

M_1	M_2	Properties of block copolymers	
		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
VIBE(38)*	*p*-(*t*-Butoxy)styrene, TBS(100)	17.5	1.08
TBS(38)	*p*-Methoxystyrene, MS(38)	12.0	1.05
MS(38)	TBS(100)	19.0	1.04

Note. Process conditions: initiating system $HI-ZnI_2$ (2:1); toluene as solvent: temperature −15 °C; 100% conversion of each monomer.
*The degree of polymerisation of the monomers is given in brackets.

Block copolymers containing alkoxy derivatives of styrene have recently been obtained using the same initiating system (Table 1). The interaction of the active sites corresponding to different $CH_2=CHOR$ monomers (where R is C_2H_5, iso-C_4H_9, or n-$C_{16}H_{33}$) with a small quantity of the bifunctional vinyl ether $(CH_2=CHOCH_2CH_2OC_6H_4)_2C(CH_3)_2$ as a cross-linking agent resulted in the formation of more complex structures such as star-shaped polymers. Polymers that were completely soluble in toluene and THF were thus obtained with the number of branches ranging from 3 to 60, controlled by the ratio of reagents and the total concentration of the living chains.[24] The value of $\overline{M}_w$ of star-shaped polymers synthesised in this manner is in the region of 2×10^4 to 3.8×10^5 with an average degree of polymerisation of the branches ranging from 38 to 114.

It was pointed out by Higashimura et al.[23,24] that the wide range of polymers synthesised provides a sound basis for their use for various practical objectives.

Let us consider two further points concerning the exact nature of the active sites occurring in the processes described in the studies of Kennedy and Higashimura. Their substantially longer lifetime compared to the carbocations formed in normal cationic systems does not make it possible to identify both these agents. The authors of these studies have taken this into account. The view of Plesch,[25,26]

according to which these processes should be classed as pseudocationic, is stated with considerable clarity in this connection. We should mention that the mechanism of pseudocation polymerisation put forward in the 1960s by Gandini and Plesch (for further details, see four studies)[25–28] is based on the concept of the covalent nature of the active sites occurring in such processes.

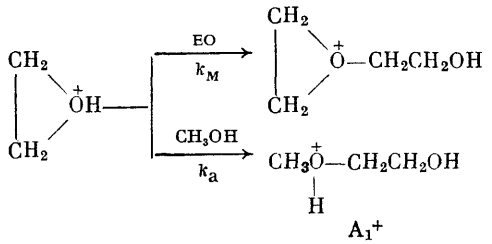
The second point, which is of a more fundamental nature, touches on the question as to whether it is legitimate to define these same active sites as living polymers. This was called into question by Sigwalt in the middle of the 1980s,[29] as was briefly mentioned in an earlier review.[1] In maintaining his point of view subsequently, Sigwalt[30] emphasised that for relatively low values of the degrees of polymerisation (in several of the cited studies they do not exceed 100) the possibility of chain transfer is not excluded, which in cationic polymerisation is usually characterised by C_M constants that do not exceed 10^{-4}. This argument is contradicted by the known facts[15] about the increase of $\overline{M}_n$ with conversion up to values of the order of 10^5 and the possibility of synthesising different block copolymers in these processes with the active sites corresponding to monomer M_1 being completely used up in the formation of products $(M_1)n-(M_2)_m$.[31,32]

Certain deviations from results of this type[1,31] merely attest to the influence of the monomer on the final effect.

2. Mechanism of the cationic polymerisation of oxygen-containing heterocycles

In recent years Penczek et al.[33–37] formulated a new mechanism for the cationic polymerisation of oxygen-containing heterocycles, which the authors called polymerisation via an activated monomer (PAM). This denotes the generation of active sites for propagation via the formation of a protonated monomer (HM^+), which then transfers the proton to a more active acceptor. The protonated acceptor then reacts with a further molecule of monomer. This sequence has been studied in detail in the case of the system $EO-BF_3-CH_3OH$, where EO is ethylene oxide.[33]

For the product HM^+ the following reactions are possible:



(5)

(6)

Route (5), which occurs provided that

$$k_M[M] > k_a[CH_3OH], \tag{7}$$

leads to active sites of the tert-oxonium ion type, namely, to a trivalent mechanism for cationic polymerisation processes of such monomers. In the presence of a nucleophile with high activity another situation is feasible, namely

$$k_M[M] < k_a[CH_3OH], \tag{8}$$

i.e., the condition under which route (6) occurs.

We should note that from the definition by Penczek et al. of route (6) as proton transfer from HM^+ to a nucleophile, this stage may be assumed to occur in two steps

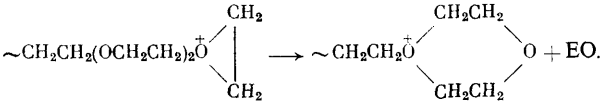
$$HM^+ + CH_3OH \underset{a}{\longrightarrow} M + CH_3\overset{+}{O}(H)H \xrightarrow{b} A_1^+. \tag{9}$$

On the basis of the greater nucleophilicity of methanol compared to EO, the authors evidently do not regard stage (9*b*) as probable and assume that there is a concerted single-stage mechanism for formation of a secondary oxonium ion. In the studies cited above this question was not considered.

The subsequent course of this process is given by the scheme

$$A_1^+ \xrightarrow{M} CH_3OCH_2CH_2OH + HM^+ \longrightarrow \underset{\substack{| \\ H \quad A_2^+}}{CH_3OCH_2CH_2\overset{+}{O}CH_2CH_2OH} \xrightarrow{M} \underset{A_2}{CH_3OCH_2CH_2OCH_2CH_2OH} + HM^+ \tag{10}$$

Its validity is supported by the formation of product A_2. As noted in one study,[33] this compound may also be formed by mechanism (5), but only together with the elimination of a 1,4-dioxan. This possibility arises for active sites of the tert-oxonium ion type which can undergo the following rearrangement:



However, in reaction mixtures obtained by polymerisation in the presence of a sufficient quantity of methanol, only a small amount of dioxan was detected.[33] From this the contribution of the PAM route could be assumed to exceed 98%.[38]

The amount of A_2 in the system, in accordance with condition (8), decreases during the process as a result of its consumption by mechanism (10). The dependence of the contribution of this route to the total process of the methanol content in the system also provides support for mechanism (6). A reduction in its content causes an increase in the role of route (5), which is suggested by the increased yield of dioxan that occurs at the same time (Table 2). The PAM mechanism starts to predominate only when there is a large concentration of methanol. The unfavourable results of these conditions for the molecular-weight characteristics of the polymers can be avoided by operating at a very low concentration of monomer, which is achieved by slow batching of it into the reaction mixture. How this is reflected in a decrease in the role of side reactions and the values of $\overline{M}_n$ of the polymers is indicated by the results of polymerisation of epichlorohydrin by the system boron fluoride–ethylene glycol with complete conversion of monomer[33] (no details were given about the other experimental conditions in this study):

Method of introducing the monomer	Yield of tetramer	$\overline{M}_n$ (calc)	$\overline{M}_n$ (experiment)
Single batch	21	2350	1530
Slow batching	0.01	2100	2100,

Results of a similar type were obtained in the polymerisation of propylene oxide (PO) in dichloromethane by $HBF_4 \cdot Et_2O$ in the presence of 1,6-hexanediol. In this case the yield of PO tetramer, which amounts to about 50% when the diol is absent, decreases to 4% when the ratio of monomer to diol is equal to 10.[36] Slow batching of monomer (0.02 ml min^{-1}) reduces the yield of tetramer to 1%. These results relate to room temperature and to a total concentration of monomer of 2.0, initiator of 5×10^{-3}, and diol of 0.2 mol $litre^{-1}$.

Table 2. Effect of methanol on the formation of 1,4-dioxan in the polymerisation of ethylene glycol by $BF_3 \cdot CH_3OH$ in dichloromethane.[33]

[M], mol $litre^{-1}$	$[CH_3OH]/[M]$	Yield of dioxan, %
1.1	2.0	1.1
1.1	3.2	13.4
1.2	6.0	39.5
1.3	17.0	66.5

Note. Process conditions: concentration of initiator 0.03 mol $litre^{-1}$; temperature 25 °C; 100% conversion of monomer.

We should note the effect discovered during polymerisation in the systems $EO-HSbF_6-CH_2Cl_2-CH_3(OCH_2CH_2)_nOH$ at 30 °C. The results presented below represent the total rate constant of polymerisation (k_t, litre mol^{-1} min^{-1}) in the presence of these hydroxyl derivatives (0.5 mol $litre^{-1}$) with a concentration of monomer and initiator of 0.5 and 4×10^{-4} mol $litre^{-1}$ respectively:[36]

n	0	1	2
k_t	8±1	13±2	22±3

This result has been interpreted by the authors as the consequence of an increase in the number of processes of type (6) as the oxygen-containing residues in the proton acceptor increase in length.

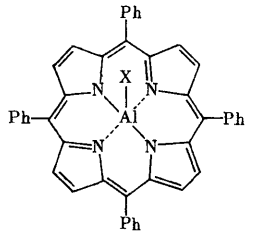
Conditions favouring a PAM mechanism can be used for the synthesis of block copolymers. This has been demonstrated[39] in the polymerisation of cyclic acetals in the presence of poly(ethylene oxide glycol) (PEOG). Thus, in the case of dioxolane and dioxepane on treatment with trifluoromethanesulphonic acid, the formation of products of the general type $HO-M_n-PEOG-M_n-OH$ and their corresponding multiblock copolymers was established.

A general review of the kinetics of PAM processes has recently appeared.[40]

III. Anionic processes

1. Initiating systems based on porphyrin

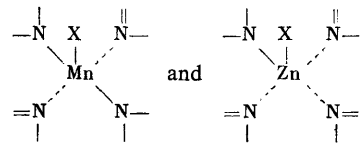
At the beginning of the 1980s the first results were published on the ability of aluminoporphyrin derivatives of the type (IV) to cause the efficient polymerisation of different types of oxygen-containing heterocycles



(IV)

In compounds (IV) the substituent can be a halogen, alkyl, OR or COOR group. These initiators will subsequently be denoted by the symbols TPhPAl–X, with substituent X being specified.

Development of these studies extended the range of initiators of a similar type and their use in the polymerisation of other monomers, including acrylic compounds.[44–48] Subsequently results were published on the initiating activity of certain tetraphenylporphyrin derivatives of manganese[49] and zinc[50,51] towards three-membered heterocycles. These compounds contain central groups that are similar to (IV)



in which X = $OCOCH_3$ in the case of manganese and X = C_2H_5, iso-C_3H_7S, or iso-C_3H_7O in the case of zinc.

Polymerisation of heterocycles. Let us first consider the validity of classifying the mechanism of these processes as anionic. The following circumstance can cast doubts in this respect. Effective polymerisation of the simplest epoxides is achieved when it is carried out in dichloromethane by the action of initiator (IV) with X = Cl. Under these conditions a cationic mechanism for the process could formally be expected. The result obtained in a model system, i.e., with an equimolar ratio of initiator and propylene oxide, would also appear to lend support to this argument. According to the PMR data, this reaction in dichloromethane gives the product $TPhPAl-OCH(CH_3)CH_2Cl$. The insertion of monomer into an Al–N bond would be more natural in anionic polymerisation. On the other hand, the further stages of chain propagation occur through polarisation of the $O^{\delta-}-Al^{\delta+}$ bond. An active $Cl^{\delta-}-Al^{\delta+}$ bond, respectively for initiation, should evidently be regarded in a similar light.

A general characteristic of initiators (IV) with different substituents X is the lack of chain termination in polymerisation caused by them and the formation of narrowly dispersed polymers with $\overline{M}_w/\overline{M}_n$ = 1.05–1.10. This relates, in particular, to epoxides[41] and lactones.[44,45] The individual nature of the initiators is most clearly revealed in the latter case. For example, the compounds

TPhP–AlCl and TPhP–AlCOOR are only active towards β-lactones, and not towards higher lactones. Compounds (IV) with an OR substituent are noted for their initiating activity towards the latter.[48,49]

The polymerisation of δ-valerolactone has been studied in greater detail, and in this case the following noteworthy effect has been identified. The low rate of polymerisation caused by the methoxy derivative of (IV) increases markedly in the presence of TPhPAl–Cl, which by itself is inert under the same conditions towards the same monomer. The scale of this effect is illustrated in Fig. 3.

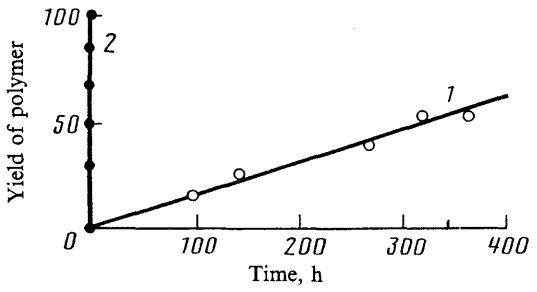


Figure 3. Polymerisation of δ-valerolactone in the absence of a solvent at 30 °C.[48] Initiators: *1*, TPhP–$AlOCH_3$; *2*, TPhP–$AlOCH_3$–TPhP–AlCl. Molar ratios: monomer/TPhP–$AlOCH_3$ = 200:1; TPhP–$AlOCH_3$/TPhP–AlCl = 2:1.

The effect of this chloride has been attributed by Aida et al.[43] to its high complexing activity towards the monomer, as was concluded from the PMR spectroscopic data. The conclusion that this type of complexation has a promoting role is consistent with the order of reaction in the absence and in the presence of this reagent:

$$v = k[\text{TPhPAl}{-}\text{OCH}_3]^2[\text{M}],$$
$$v = k'[\text{TPhPAl}{-}\text{OCH}_3][\text{TPPhAl}{-}\text{Cl}][\text{M}].$$

The effects revealed in a study of the interaction of the active sites corresponding to these initiators with typical deactivators of anionic chains (HCl, ROH, H_2O, etc.) are unusual. In these systems deactivation of the active sites occurs at the same time as regeneration of the initiator, for example

$$\text{TPhAl}{-}\text{M}_n{-}\text{Cl} \overset{\text{HCl}}{\rightleftarrows} \text{TPhPAl}{-}\text{Cl} + \text{H}{-}\text{M}_n{-}\text{Cl}.$$

The high frequency of these exchanges, exceeding the rate of propagation, leads to results that are typical of polymerisation via living chains. This is achieved by the introduction of a mixture of proton donor and monomer into a solution of initiator. Several examples are given in Table 3. A second portion of monomer introduced after complete conversion of the initial portion results in an increase in the molecular weight of the polymer while retaining a narrow molecular weight distribution. This result has been obtained in particular for the system PO–TPhPAl–Cl–CH_2Cl_2–CH_3OH; the final value of $\overline{M}_w/\overline{M}_n$ in this case was 1.09.

Similar results were obtained in the polymerisation of lactones and also with the introduction of a "foreign" monomer into the reaction mixture at the second stage of the process. An EO–PO block copolymer was synthesised in this manner.

Table 3. Polymerisation in R–CH(O)–CH_2–TPhPAl–Cl–CH_3OH systems in the absence of a solvent.[48]

R	Time, h	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
H	48	700	1.05
CH_3	48	1300	1.08
CH_3CH_2	96	1200	1.10
CH_2Cl	48	1500	1.04

Note. Process conditions. Molar ratios: monomer/initiator = 200, methanol/initiator = 9; room temperature; 100% conversion of monomer.

On the basis of these characteristics, Inoue et al.[45] introduced the term "immortal polymerisation" for such processes.

Similar effects were recently found in systems incorporating zinc derivatives of tetraphenylporphyrin. This was demonstrated, in particular, for the polymerisation of PO by the system TPhP–$Zn(C_3H_7)S$–CH_3OH. In this case the value of $\overline{M}_w/\overline{M}_n$ corresponding to 100% conversion of monomer was 1.08.

The molecular-weight characteristics suggest that the rate of exchange between active sites and proton donor molecules is much higher than the rate of propagation.

Polymerisation of polar unsaturated monomers. Some of the initiators under discussion have proved active towards methacrylates, but only in the light, according to the original findings.[42] It was subsequently shown to be possible to carry out polymerisation also in the dark provided that initiators (IV) with substituents X = OR or SR were used.[46] An example of this is the polymerisation of methyl methacrylate (MMA) in dichloromethane at 35 °C by TPhP–$AlSC_3H_7$. With a ratio of MMA:(IV) = 200:1 and complete conversion of monomer, a polymer with $\overline{M}_n = 2.2 \times 10^3$ and $\overline{M}_w/\overline{M}_n = 1.12$ was obtained.

Use of initiator (IV) with X = SPh achieves results of a similar type. A linear dependence of $\overline{M}_n$ on the degree of conversion and formation of polymer with $\overline{M}_n = 3 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 1.1$ has been established in this case.

Information on nitrile monomers is currently limited to data on the polymerisation of methacrylonitrile (MAN) by propagating MMA chains. An MMA–MAN block copolymer was obtained in this case.

We should note that the possibility of polymerising these monomers in the dark depends not only on the nature of the initiator but also on the selected reaction temperature. Thus,

polymerisation of PO by TPhPZn–SC_3H_7 occurs in the light at 25 °C but is also achieved in the dark at 70 °C; the $\overline{M}_w/\overline{M}_n$ values in these cases were 1.05 and 1.07 respectively.[51]

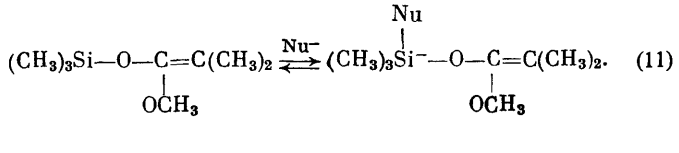
2. Group transfer polymerisation

The first publication of Webster et al.[52] concerning a new method of anionic polymerisation, established under the name of group transfer polymerisation (GTP), appeared in 1983. The mechanism of GTP differs fundamentally from other known polymerisation processes in that each stage of addition of the next monomer molecule to the growing chain combines initiation and propagation, concluding with reproduction of the structure that in principle matches that of the original initiator.

The method is based on the use of mixtures of *O*-silyl ketals of ketenes with nucleophilic or electrophilic compounds. According to the accepted terminology, the first of these components are called initiators and the second are known as catalysts. Nucleophiles such as HF_2K, $FNBu_4$, and certain others or electrophilic compounds of the Lewis acid type such as zinc halides can function as catalysts. Nucleophilic catalysts have proved more convenient for the polymerisation of methacrylates, to which most of the studies on GTP have been devoted.

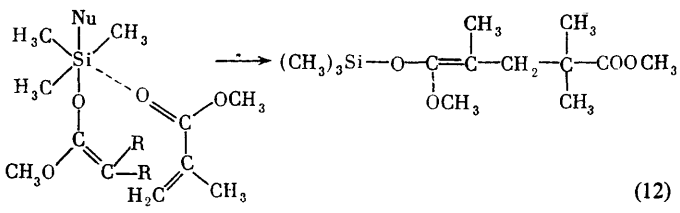
An important advantage of these processes over polymerisation of the same monomers using conventional anionic initiators (organometallic compounds) is that propagation of the living chains is not complicated by side reactions† even at room temperature. This characteristic of GTP considerably simplifies the synthesis of narrowly dispersed polymers—a task of considerable practical significance. Even with the normal technique (simultaneous introduction of the whole portion of monomer into the reaction mixture), $\overline{M}_w/\overline{M}_n$ for the MMA polymers is equal to 1.3, while with slow batching of the monomer, $\overline{M}_w/\overline{M}_n$ = 1.01. This property has substantially simplified the synthesis of block copolymers of different methacrylates, including hybrid macromolecules of the type A–B–C.

The scheme put forward by Webster et al.[54,55] to interpret the mechanism of GTP involves the formation of a pentacoordinate silicon derivative in the reaction between initiator and catalyst, which has been demonstrated for the simplest example of ketene *O*-silyl ketals and a nucleophile (Nu^-), which may be an F^- or HF_2^- ion.



(11)

The product of this reaction interacts with the monomer to form an intermediate hexacoordinate silicon derivative, rearrangement of which completes the propagation step. We can illustrate this in the case of methyl methacrylate (MMA), where R = CH_3:



(12)

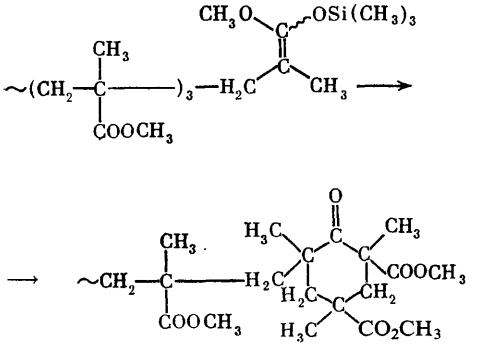
† The mechanism and results of these reactions are examined in detail in another review.[53]

The existence of an intermediate has not been confirmed experimentally, but the results of nonempirical calculations, referred to in a study by Müller,[56] provide evidence for it. However, the conclusion that there is a combination of initiation and propagation steps at each stage of the insertion of monomer into the polymer chain is valid. The final product of reaction (12) interacts with the nucleophile according to scheme (11), thus achieving the further progression of polymerisation.

In practice, tris(dimethylamino)sulphonium difluoride (DSDF) has been used to a relatively greater extent than other nucleophiles. Amongst the reaction products in systems in which it involved, triple block copolymers of MMA with n-butyl and allyl or glycidyl acrylates have been synthesised. Kinetic studies were carried out with DSDF and the simplest of the ketene *O*-silyl ketals. Let us consider the results of Müller et al.[57]

Standard conditions were selected: THF as solvent, temperature 20 °C, concentrations of monomer, initiator, and catalyst equal to 0.18, 1×10^{-3}, and 2×10^{-6} mol litre^{-1} respectively. One of these parameters was varied, keeping the remaining conditions constant. With a concentration of catalyst $\leqslant 3 \times 10^{-6}$ mol litre^{-1}, rapid initiation occurred with a propagation reaction that was first-order with respect to this reagent. With a concentration of catalyst $> 3 \times 10^{-5}$ mol litre^{-1} the initial stage of polymerisation was characterised by an induction period and the rate of reaction then passing through a maximum. However, the decrease in rate of polymerisation due to termination stages did not prevent the complete conversion of monomer. When the concentration of initiator was varied, similar effects—an induction period and a curve with a maximum on the conversion/time coordinates—occurred in the region of higher concentrations of this reagent. The authors assume that in this case these are due to the deactivating effect of excess initiator rather than as a result of termination.

A study by Brittain and Dicker,[58] in which the behaviour of short-chain oligomers of this type was studied under standard conditions, has shed light on the question of the mechanism of termination reactions in GTP processes. MMA–(1-methoxy-2-methyl-1-propenyl)oxytrimethylsilane (P_1^*) was chosen as the initial system, with ratios of MMA/P_1^* equal to 2 and 3. Under the conditions employed (THF, tetrabutylammonium dibenzoate as catalyst, room temperature) oligomerisation of MMA is complete after 2 min. The IR characteristics of deactivated samples of the reaction mixture taken after different intervals of time indicated a gradual decrease in intensity of the absorption band due to the C=C bond (1687 cm^{-1}) together with the appearance and increase in intensity of an absorption band due to a carbonyl group (1716 cm^{-1}). These effects were attributed to intramolecular cyclisation of the active sites:[58]



In a determination of the rate of cyclisation of the oligomers based on the change in intensity of these bands, good agreement was obtained for the results calculated for each of the IR properties: 0.009 and 0.010 mol litre^{-1} s^{-1} for the C=O and C=C groups respectively. The authors emphasised that the role of this reaction is important only in the absence of monomer. According to their results, under real polymerisation conditions the ratio of the rate of propagation to the rate of deactivation by this mechanism is 2600.[58]

Of the other monomers that display an ability to undergo GTP, acrylates, methyl vinyl ketone, acrylonitrile, and pentadiene- and hexadiene-carboxylate esters are mentioned in the literature.

GTP processes are of definite practical value because of the possibility of using such initial reagents that can be used to synthesise polymers with reactive terminal groups. In particular, initiators containing the group $\geqslant C(OSi(CH_3)_3)O(CH_2)_2OSi(CH_3)_3$ are of this type. On hydrolysis of the polymers obtained by GTP involving these initiators, macromolecules with terminal OH groups are formed.

An interesting development for GTP processes was made in a study by Miller et al.,[59] the subject of which was an investigation of the possibility of extending the rate of nucleophiles through the reaction of different crown ethers with alkali metal salts. This was successfully carried out in the case of a system containing $(CH_3)_3Si-O-C=\underset{OCH_3}{C(CH_3)_2}$, dibenzo-18-crown-6, and potassium acetate. When the crown ether was absent, this system was inert towards MMA, whereas by using a three-component system with this composition it was possible to obtain PMMA in 92% yield with $\overline{M}_w/\overline{M}_n$ = 1.9 (acetonitrile as solvent, temperature 50 °C).

A comprehensive description of the experimental details of the synthesis of the initial reagents, the effects on GTP of varying them, and the characteristics of the resulting polymers appear in a study.[55] Replacement of Si initators by their Sn and Ge analogues is included amongst the points mentioned in it.

A detailed comparison of the process characteristics of normal anionic polymerisation of methacrylates and the behaviour of the same monomers in GTP processes has been carried out by Müller.[56,60] The distinct nature of the latter does not prevent them from being classified under the general title of anionic-type reactions.

IV. Processes initated by Ziegler–Natta catalysts

In the Russian literature of recent years that has been devoted to problems of catalytic polymerisation,[61–64] there has been no review of the polymerisation of olefins by homogeneous Ziegler catalysts, which has undergone a particular rapid development during these years.

At the early stage of research into these processes, homogeneous systems were regarded as a convenient subject for studying the mechanism of polymerisation. For a long time they had no practical use, since all of the known systems of this type were considerably inferior to heterogeneous systems of a similar nature, differing from them through having much lower values of the rate constants of propagation and by their inability to form stereoregular polymers.

At the beginning of the 1980s the development of homogeneous Ziegler systems acquired a "second wind" as a result of the production of catalytic complexes of extremely high activity, surpassing the activity of heterogeneous systems of the same type. The replacement of aluminium alkyl and haloalkyl compounds, which were extensively used as components of a large number of Ziegler–Natta catalysts, by aluminoxanes in combination with derivatives of certain transition metals led to this situation.

The first results on highly active soluble catalysts of this type were obtained by Sinn, Kaminsky et al.[65,66] for systems containing aluminoxanes and zirconium or titanium compounds. In particular, in the polymerisation of ethylene by an initiating system based on a cyclic methylaluminoxane containing 10–20 $OAl(CH_3)$ groups and the compound $Cp_2Zr(CH_3)_2$, where Cp = cyclopentadienyl, the value of the propagation constant k_p was 10^5 litre mol^{-1} s^{-1} (data for 90 °C).[67] It is approximately 10^4 times higher than those values which are known for conventional homogeneous initiating systems and $10^1-10^{1.5}$ times higher than the kinetic parameters relating to heterogeneous catalysts.[68] The relative activity of certain other systems based on the same type of aluminoxane are briefly indicated by the data in Table 4.

Table 4. Polymerisation of ethylene by soluble complexes of methylaluminoxane with compounds of Group IV metals with a constant pressure of monomer.[67]

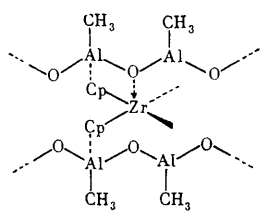
Compound	Concentration, mol litre^{-1}	t, °C	Activity of system, g polymer (g M*)$^{-1}$ h 100 kPa
$Cp_2Ti(CH_3)_2$	$3\cdot10^{-6}$	20	500
$Cp_2Ti(CH_3)Cl$	$3\cdot10^{-6}$	20	50 000
$Cp_2Zr(CH_3)_2$	$1\cdot10^{-7}$	20	9 000
$Cp_2Zr(CH_3)_2$	$1\cdot10^{-7}$	70	700 000
Cp_2ZrCl_2	$3\cdot10^{-8}$	70	1 000 000
$Cp_2Hf(CH_3)_2$	$3\cdot10^{-8}$	70	60 000

Note. process conditions: concentration of aluminoxane based on a single unit 1.5×10^{-2} mol litre^{-1}; monomer pressure 800 kPa.

*Transition metal.

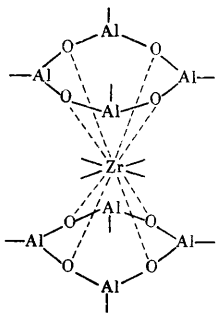
We should note the considerably higher concentration ratio of Al to transition metal in these examples compared to those normally used in Ziegler processes. The above-mentioned high efficiency of the alumino-zirconium system is provided by the very small concentration of the transition metal compound but only with a large excess of aluminoxane (see Table 4). When its concentration is reduced to a value exceeding that of the zirconium component even by a factor of 10^2-10^3, the activity of the system decreases sharply.[66]

On the basis of this phenomenon, Kaminsky et al.[66] attributed to the active agents structure (V), the formation of which requires a large excess of aluminoxane.

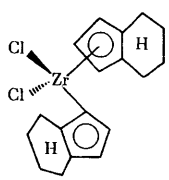


(V)

The kinetics of formation of the catalytic complex, corresponding to first and second order with respect to the zirconium and aluminium components respectively, are consistent with this. We should note, however, that structure (V) has no experimental support, although it seems plausible for linear aluminoxanes. For cyclic aluminoxanes it is necessary to take into account the increase in promoting effect of these compounds together with the increase in the number of >Al—O— residues contained in it.[65] It may be assumed from this that polyligand structures are formed in systems involving cyclic aluminoxanes, as is shown schematically in the case of a four-unit aluminoxane:[69]



Many of the same catalysts have been used for efficient polymerisation of propylene,[67] but it was only possible to improve on the synthesis of atactic polymers when a zirconium bis(indenyl) derivative with ligands rigidly connected by an ethylene bridge was used:[70]



The use of the *l*-enantiomer of this compound in combination with methylaluminoxane resulted in the formation of polypropylene with the following properties (toluene as solvent, temperature 10 °C)

Fraction*	Content of isotactic triads, %	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-3}$
Soluble in boiling heptane	96.0	1.77	4.96
Insoluble in boiling heptane	98.6	8.90	22.78

*Relative proportions of the fractions not indicated.

The above results contradict the idea that the use of insoluble Ziegler—Natta complexes is obligatory for carrying out the stereospecific polymerisation of olefins.

Recently Kaminsky[71] prepared a number of novel catalysts based on chiral zirconocenes in combination with methylaluminoxane that effected the synthesis of isotactic polyolefins. Some of these catalysts for the first time opened up the possibility of the polymerisation of cyclic olefins (cyclobutene, cyclopentene, etc.) without the complication of ring opening.

The studies of Kaminsky and Sinn[65—67,70,71] do not contain the physicochemical characteristics of the catalysts mentioned. Let us therefore introduce the data of Fink et al.[72,73] that relate to one of the simplest homogeneous aluminotitanium systems, namely, $Cp_2TiEtCl-EtAlCl_2$. They are worthy of attention mainly because they provide the first direct evidence for the insertion of monomer into the bond of the carbon atom of the active site with a transition metal. This follows from a detailed analysis of the ^{13}C NMR spectra of this system in the absence and in the presence of ethylene.[73] Kinetic studies by the same authors, which suggest that there is a two-stage mechanism for formation of the active sites in systems of the general type $Cp_2TiRCl-EtAlCl_2$, where R = alkyl, are of considerable interest.[74—76] This conclusion is based on the lack of initiating activity in the 1:1 complex indicated below as C_1:

$$Cp_2TiRCl + {}^1/_2(EtAlCl_2)_2 \overset{K_1}{\rightleftarrows} C_1. \qquad (13)$$

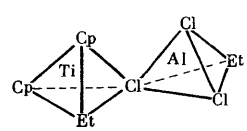
Only when it reacts with an excess of the aluminium component does it give rise to the formation of an active site (C*), which is accompanied by the formation of a dimeric aluminium derivative (Al_2') of an undetermined nature

$$C_1 + (EtAlCl_2)_2 \overset{K_2}{\rightleftarrows} C^* + Al_2'. \qquad (14)$$

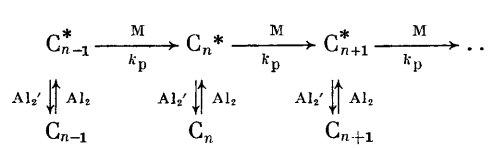
According to Eqns. (13) and (14), an increase in the original ratio of Al to Ti increases the initial rate of polymerisation of ethylene.

From the intensity of the ^{13}C NMR signals due to the $Ti-CH_2$ group, limiting values of $5 \times 10^{-3} \geqslant K_1 \geqslant 5 \times 10^{-4}$ litre mol^{-1} at −33 °C have been calculated for the equilibrium constants of Eqn. (13), while for K_2 a value of the order of 10^{-3} litre mol^{-1} was obtained.

The results that followed from an analysis of the ^{13}C NMR spectra (reduction in electron density on the titanium atom, absence of bridging methylene groups) led the authors to conclude that the C_1 complex probably exists in the form of the structure



The results of studies by Fink et al.[74—76] were used for mathematical simulation of the processes studied, which by neglecting chain termination and chain transfer made it possible to determine the rate constants of the successive propagation steps corresponding to the scheme



According to the calculations carried out, the value of k_p depends on the size of R up to R = C_5H_{11} in the component Cp_2TiRCl (data for ethylene at 283 K):[76]

Reaction	$C_2 \xrightarrow{M} C_4$	$C_3 \xrightarrow{M} C_5$	$C_4 \xrightarrow{M} C_6$	$C_5 \xrightarrow{M} C_7$	$C_6 \xrightarrow{M} C_8$
k_p, litre mol^{-1} s^{-1}	120—140	96	62	48	47.

By using a flow method with a rate of flow 2 m s^{-1} that made it possible to control the kinetics of oligomerisation and starting with a reaction time equal to 0.095 s, it was possible to characterise the dependence of the rate of the process on the concentration of monomer while retaining homogeneity of the reaction mixture. As a result the reaction was established as first-order with respect to monomer.[76]

* * *

Each of the trends in research examined here has developed rapidly, considerably strengthening ideas about the mechanism of the formation of macromolecules in ionic systems. Of no less importance are the studies reviewed here on the synthesis of polymers with practical value. This relates in particular to the preparation of various block and multiblock copolymers based on the use of different types of novel initiating systems.

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