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The Mechanism of the Initiation of the Radical Polymerisation of Polar Monomers in Systems Comprising Organometallic Compounds

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In the present review an attempt is made to examine from the same standpoint the reactions responsible for the development of radical polymerisation in systems comprising organometallic† compounds in combination with oxygen-containing derivatives (oxygen, hydroperoxides, acyl peroxide) or derivatives of variable-valence metals. Attention has been concentrated on systems effective at a low temperature. The causes responsible for the inhibition or total suppression of ionic-coordination polymerisation of polar monomers and favouring the development of the radical process in systems of the Ziegler-Natta type have been discussed. The bibliography includes 135 references.

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I. INTRODUCTION

An attempt has been made to use Ziegler–Natta catalysts, which have been successfully employed for the polymerisation of α-olefins, to polymerise other monomers, in particular polar monomers of the vinyl series. At first these attempts were unsuccessful: monomers such as vinyl acetate, methyl methacrylate, acrylonitrile, etc. could not be polymerised. Attempts were made to account for the absence of polymerisation by the breakdown of the catalyst in its interaction with the monomer. The development of studies on the interaction of these catalytic systems with vinyl monomers led to the creation of new initiating systems based on organometallic compounds and oxygen or peroxides capable of inducing radical polymerisation at reduced temperatures. On the other hand, the subsequent employment of the so called modified Ziegler catalysts also made possible the polymerisation of polar monomers.

II. SYSTEMS WITH AN ORGANOMETALLIC COMPOUND (OMC) AND AN OXYGEN-CONTAINING DERIVATIVE

1. Systems with an Organometallic Compound and Oxygen or a Hydroperoxide

It has been shown in a number of studies[1-12] that organic derivatives of Group II and III elements (zinc, cadmium, boron, and aluminium) alone give rise to hardly any polymerisation of polar monomers of the vinyl series; an effective process developed only in the presence of oxygen or peroxy-compounds.

The data presented in Tables 1 and 2 show that the most active of the systems investigated are those containing organoboron compounds in combination with oxygen or a hydroperoxide. The organoboron compounds can be arranged in the following sequence in terms of their activity[13]:

$$(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2 > B(n\text{-}C_4H_9)_3 > (n\text{-}C_4H_9)_2B(n\text{-}C_4H_9O) > (n\text{-}C_4H_9)_2BBr > (n\text{-}C_4H_9)_2BCl$$

The overall activation energy found for a number of systems proved to be very low and comparable to the activation energy for the chain propagation reaction, which made it possible to carry out the process at reduced temperatures[8,12,14-16].

The copolymerisation constants obtained for a number of monomers suggested that radical polymerisation takes place in these systems[2,6,13,16,18,19].

Table 1. Polymerisation of polar monomers under the influence of the systems organometallic compound–oxygen.

Monomer	Process conditions: initiator type	initiator concn., M	10^2 × molar ratio O_2:OMC	time, h	t, °C	Yield of polymer, %	References
VA	$B(C_2H_5)_3$	$2.7\cdot10^{-3}$	14.3	20	30	40	13
MMA	ditto	$8\cdot10^{-2}$	6.5	~0.5	30.1	14	14
VC	$B(C_4H_9)_3$	$1.8\cdot10^{-2}$	9.5	3	20	20	15
AN	ditto	$4\cdot10^{-2}$	**	~0.8	0	4.2	16
VA	$Al(C_2H_5)_3$	$7\cdot10^{-2}$	50	24	25	12	4
VC	ditto	5*	***	4	−17	3	9
MMA	$Cd(C_2H_5)_2$	$5\cdot10^{-3}$	6.9	21	20	14	17

VA = vinyl acetate; MMA = methyl methacrylate; VC = vinyl chloride; AN = acrylonitrile.

*The concentration of $Al(C_2H_5)_3$ in petrol is expressed as a weight percentage; molar ratio VC : $(C_2H_5)_3Al$ = 7.28 : 1.

**In a sealed tube in air.

***Experiment carried out in a stream of dry and purified air flowing at a constant rate (50 ml min^{-1}).

Welch[2] believes that radicals cannot form as a result of the thermal decomposition of organometallic compounds of this type, since the polymerisation temperature is much below the range corresponding to the thermal decomposition of zinc and cadmium alkyls and boron and aluminium

† The Russian authors use the work "organoelemental" but since the term is not familiar in English and most of the compounds discussed are in fact metal derivatives, it has been replaced by "organometallic", especially since this is the term actually used in the title in the Russian version also (Ed. of Translation).

alkyls altogether fail to yield free radicals on thermal decomposition. The fact that the process can be carried out only in the presence of oxygen or peroxides[20] suggests that the stage preceding the generation of free radicals is the formation of peroxy-derivatives of the organometallic compounds.

Table 2. Polymerisation of vinyl chloride under the influence of the systems organometallic compound–peroxide[15].

Process conditions				Conversion, %	Degree of polymerisation	Activation energy, kcal mole^{-1}
catalyst, mole %	cocatalyst* mole %	t, °C	time, h			
$B(C_2H_5)_3$	13	room	several min	explosion		
1,79	42	−55	4	22.7	560	
	50	−65	68	61.4	400***	
	50**	−55	4	19.6	820	
$Al(C_2H_5)_3$	23	30	1	15.4	450	
1,89	50	−20	4	5.4		12.8
$Cd(C_2H_5)_2$	48	32	4.8	10.0		
2,5	»	22	19.0	10.0		16.0
	»	0	25.0	3.5		
$Zn(C_2H_5)_2$	48.5	4	1.5	25.6		
2,52	»	3	2.0	16.1		9.6
	»	−10	2.5	4.7		

*Cumenyl hydroperoxide, mole % relative to the catalyst.

**The part dissolved in tetrahydrofuran.

***t-Butyl hydroperoxide.

The synthesis and reactions of the organometallic compounds have been examined in detail by Sosnowsky and Braun[21], and therefore we shall note only some of their most important (as regards the present topic) reactions. The monoperoxides of cadmium, zinc, boron, and aluminium are extremely unstable at normal temperatures and readily undergo a number of heterolytic and homolytic reactions:

$$-MOOR- \xrightarrow{-MR} 2-MOR \quad (1)$$

$$-MOOR- \longrightarrow -M(OR)_2 \quad (2)$$

$$-MOOR- \longrightarrow -MO^{\cdot} + {}^{\cdot}OR \text{ (or } -MOO^{\cdot} + R^{\cdot}) \quad (3)$$

Alkoxy-derivatives are formed as a result of intermolecular exchange with the initial organometallic compound [reaction (1)][22-25] or by intramolecular exchange [reaction (2)][26,27].

Compounds which might form as a result of further reaction of the free radicals [reaction (3)] have also been identified[23]. The mixture of products formed in the presence of the peroxides of trivalent elements is still more complicated, since diperoxides can also participtae in reactions (1)–(3). For example in the oxidation of organoboron compounds homolytic decomposition takes place to the greatest extent precisely at this stage[23]. A general parallel may be drawn[28] between the ease of the auto-oxidation of organoboron compounds and the capacity of any group to transfer electrons to the unfilled boron orbital, making it less sensitive to attack by oxygen. The activity series of organoboron compounds,

$$BR_3 > R_2BOR > RB(OR)_2 \text{ and } BR_3 > R_2BCl > RBCl_2$$

in oxidation reactions are determined by the overlapping of the boron orbitals by those of chlorine or oxygen. The reactivity of organoboron compounds in oxidation corresponds to their activity in polymerisation processes[13]. The oxidation of organoaluminium compounds and further reactions of peroxides take place even more vigorously than with organoboron compounds[23,27,29]. The only stable peroxides proved to be $Al(OR)_2OOR$, which were isolated and characterised[30]. The fact that the reactions of the peroxy-derivatives of organoaluminium compounds involve a stage with formation of free radicals was demonstrated under model conditions[4] and confirmed by showing that polymerisation in the presence of these peroxides is possible[30]. The peroxy-compounds obtained beforehand at a low temperature are then capable of initiating polymerisation when the monomer is introduced[31]. However, the activity of these pre-formed peroxides is much lower than that of systems which initiate polymerisation by peroxides *in statu nascendi*. In the first case the process develops at temperatures normal for radical initiation‡ and in the second it actually takes place at very low temperatures down to −65°C (for example, with boron compounds).

This phenomenon was explained by the existence of "active" peroxide, since it was established that ethereal solutions of the peroxide rapidly lose their catalytic activty although the peroxide concentration determined iodometrically did not change[31]. It was suggested that the low-temperature polymerisation is initiated by the free radicals formed as a result of a kind of redox reaction between the initial organometallic compound and its peroxide[9,14,33-35].

Bawn et al.[33] showed that in the polymerisation of methyl methacrylate in the presence of $(C_4H_9)_3B-O_2$ neither the peroxide (obtained from part of the boron alkyl) nor the organoboron compound by itself are capable of initiating the low-temperature polymerisation. In a kinetic study they established the following dependence of the reaction rate on the concentrations of the monomer, peroxide, and the initial boron alkyl:

$$V = k_{obs}[M][ROOBR_2]^{1/2}[Br_3]^{1/2}.$$

A mechanism for the formation of free radicals was proposed on the basis of the hypothesis that the reaction is a free radical process. Initially a monomer–boron alkyl complex is produced:

$$BR_3 + M \rightleftarrows BR_3^{\cdot}M. \quad (4)$$

Equilibrium is established rapidly and is displaced to the right so that the concentration of the complex is almost equal to the initial concentration of tributylboron. Then, in bimolecular redox reaction (5), the initiating radicals are produced:

$$BR_3^{\cdot}M + R_2BOOR \rightarrow R_3BMRO^{\cdot} + R_2BO^{\cdot}. \quad (5)$$

The authors assume that chain propagation and termination take place as in an ordinary free radical process. The dependence of the rate of initiation on the concentrations of the initiator components obtained from Eqns. (4) and (5) and the variation of the overall rate of the process with the same concentrations found on this basis agree with the experimental findings. These hypotheses might be confirmed by data on the polymerisation kinetics of monomers of low polarity, in particular vinyl chloride. Then the equation for the rate of the process should differ from the corresponding expression for highly polar monomers. Unfortunately Bawn et al.[33] do not present data of this kind.

Talamini and Vidotto[8] believe that the monomer does not participate in the initiation step, since the activation

‡ The period of 50% decomposition of a 1% solution of boron peroxide in octane is 4.3 and 1.5 h at 50° and 100°C respectively; at 25°C the content of the peroxide does not change over a period of 50 h.[32]

energy for initiation under the influence of $(C_4H_9)_3B-O_2$ is the same in the polymerisation of vinyl chloride (a monomer of low polarity) and the highly polar methyl methacrylate§.

Welch[14] believes that the redox reaction between the oxidised and unoxidised forms of the organoboron compound does not require the initial formation of the complex of R_3B with the monomer. The experimental findings for polymerisation agree with the proposed mechanism for the generation of free radicals: the overall rate of the process and the conversion are higher when the concentrations of the boron alkyl and oxygen do not differ very much:

$$BR_3 + O_2 \rightarrow R_2BOOR, \quad (6)$$

$$BR_3 + R_2BOOR \rightarrow BR_3 + R_2BO^{\cdot} + RO^{\cdot}. \quad (7)$$

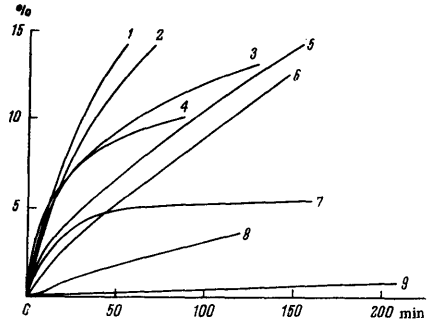


Figure 1. Polymerisation of methyl methacrylate at 30°C in the presence of a constant concentration $[(C_2H_5)_3B]_0 = 7.18 \times 10^{-3}$ M and a variable concentration $[O_2]_0$ (10^{-3} M): 1) 3.36; 2) 1.97; 3) 4.47; 4) 1.14; 5) 5.4; 6) 6.65; 7) 0.51; 8) 7.89; 9) 0.0.

When $[O_2] \gg [R_3B]$, the entire boron alkyl is oxidised to the peroxide and reaction (7) is impossible. When the concentration ratio is reversed, the peroxy-compound is rapidly exhausted, which leads to the decay of the process at a low conversion. From a study of the polymerisation kinetics of methyl methacrylate with $(C_2H_5)_3B-O_2$, Hansen[34] showed that the process can be described by simple relations only at the very beginning. This is because in systems of this type a number of competing reactions take place and lead to the formation of free radicals. The rates of these reactions are different and are determined by the relative amounts of the starting reactants. Figs. 1 and 2 present the kinetic curves obtained for various concentrations of one of the initiating components. The maximum rate occurs when $[R_3B] > 2[O_2]$, but it then falls rapidly as a result of the complete reduction of the peroxide. Under the condition $[O_2] < [R_3B] < 2[O_2]$ the system contains, together with the initial boron alkyl, its hydroxy-form, which is a weaker reducing agent and gives rise to slow and prolonged generation of free radicals at a constant rate:

$$\rangle BOOR + \rangle BR \xrightarrow{fast} R^{\cdot} + (BO^{\cdot}) \quad (8)$$

$$\rangle BOOR + \rangle BOR \xrightarrow{slow} R^{\cdot} + (BO^{\cdot}). \quad (9)$$

The homolytic dissociation of the peroxide bond as a result of the redox reaction was studied under model conditions by Hansen and Hamann[37]. When iodine was used as a free radical acceptor, they established that the interaction of the peroxide with the unoxidised boron alkyl is a reduction process with a stoichiometric ratio close to unity. The formation of ethyl radicals (the only ones reliably demonstrated) does not take place in each step of the interaction in consequency of reduction in the "cage":

$$\begin{array}{l} \quad\quad B{-}C_2H_5 \\ \quad\quad\quad\uparrow \\ C_2H_5O{-}O{-}B\langle \end{array} \rightarrow \rangle B{-}OC_2H_5 + C_2H_5^{\cdot} + \rangle BO^{\cdot}. \quad (10)$$

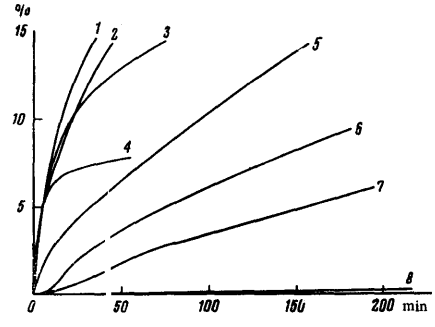


Figure 2. Polymerisation of methyl methacrylate at 30°C in the presence of a constant concentration $[O_2]_0 = 5.4 \times 10^{-3}$ M and a variable concentration $[(C_2H_5)_3B]_0$ (10^{-3} M): 1) 21.5; 2) 71.8; 3) 14.3; 4) 35.5; 5) 7.18; 6) 5.38; 7) 3.6; 8) 1.43; 9) 0.0.

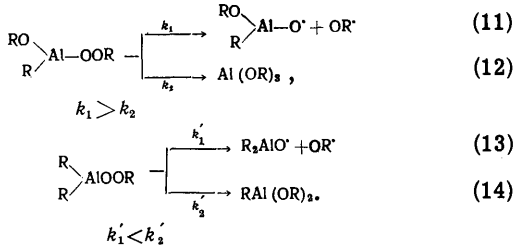
The emergence of the radicals from the "cage" initiates the free-radical processes; the reaction in the "cage" results in the formation of alkoxy-compounds. In agreement with the data obtained under model conditions, a very small boron content was found in the polymer[34].

Furukawa and coworkers[31] showed that systems based on alkoxy-derivatives of zinc in combination with peroxides are more active than those based on zinc alkyls. The latter are weak Lewis acids[38]; this is even more true of the alkoxy-derivatives of zinc, which makes it unlikely that its complex with an electron-donor monomer is formed as a result of reaction (4).

The findings for systems with organoaluminium compounds suggest that in this case too the active polymerisation initiators at low temperature are systems based on monoalkoxydialkylaluminium and oxygen or a hydroperoxide This is confirmed[9,35] by the absence of the polymerisation of vinyl chloride when the system $(C_2H_5)_3Al-O_2$ contains little oxygen and the impossibility of the polymerisation of vinyl acetate under the influence of the system $(C_2H_5)_3Al$–isopropylphenyl hydroperoxide[4]. These findings show that, of the two possible modes of the process: decomposition with formation of free radicals or rearrangement into

§ In the determination of the activation energy for the initiation reaction the value $E_{prop} - \frac{1}{2}E_{term} = 1.5$ kcal mole^{-1} was employed[8]. However, the value of $E_{prop} - \frac{1}{2}E_{term}$ found for vinyl chloride in a number of studies varied from 1.5 to 5 kcal mole^{-1}, [36] and therefore the identity of the activation energies for the initiation reaction found by Bawn[33] and Talamini[8] is purely fortuitous.

an alkoxy-compound, the first takes place with organic derivatives of alkoxyperoxyaluminium [reaction (11)] and the second takes place with the alkylperoxy-derivatives [reaction (14)]:



(11)

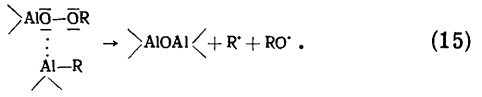
(12)

(13)

(14)

This kind of inversion of rate constants can be explained by the fact that the RO group reduces the electron deficit of the aluminium atom and thus electrons are shifted to the peroxide bond, facilitating its dissociation. On the other hand, in the alkyl peroxide the withdrawal of electrons from the peroxide bond hinders its dissociation and, together with the electron-acceptor properties of the aluminium atom, leads to rearrangement with formation of an alkoxy-derivative. These hypotheses can explain the experimental observations regardless of whether the decomposition of the peroxide is a mono- or bi-molecular process.

Razuvaev and coworkers [35] attributed the formation of free radicals to a redox reaction of the type



(15)

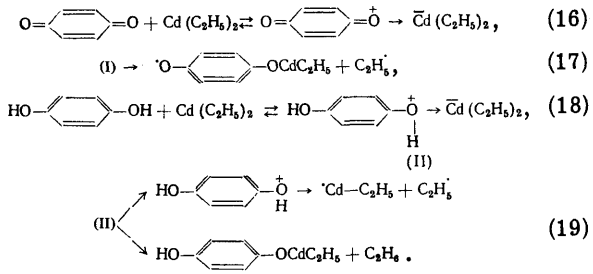
The formation of the R$^{\cdot}$ radical (R = ethyl) was confirmed by the analysis of the gaseous compounds evolved; the RO$^{\cdot}$ radicals were detected in the form of the terminal groups in the polymer.

The results show that the conclusion that polymerisation with organometallic compound–oxygen or hydroperoxide systems has a radical mechanism is fairly well founded. However, the chemistry of the initiation process, in particular the nature of the initiating radicals and the participation of the monomer in this reaction, involves many contradictions. We may note that in the absence of oxygen, boron alkyls are capable of initiating very slow polymerisation of styrene, acrylonitrile, and 1,1-dichloro-2-fluoroethylene, but not vinyl acetate [3].

Hydroquinone does not inhibit this process, which, according to Hansen [34], is evidence of the occurrence of ionic polymerisation. The polymerisation of methyl methacrylate under the influence of (iso-$C_4H_9)_3Al$ and (iso-$C_4H_9)_2Al.(iso\text{-}C_4H_9O)$ takes place in the absence of oxygen at 60°C and an initiator concentration of 10 mole % relative to the monomer [39]. It was shown that the polymerisation of methyl methacrylate also takes place with $(C_2H_5)_3Al$. [40] The poly(methyl methacrylate) formed has a structure characteristic of polymers produced under the influence of $(C_2H_5)_4CaZn$ and (n-C_4H_9)Li. [41] We may note that extremely large amounts of the catalyst (up to 30% relative to the monomer) are employed in these investigations [39,40]. This leads to the binding of a considerable proportion of the monomer in a complex with the organoaluminium compound (via the carbonyl oxygen), which results in a decrease of electron density at the double bond. Under these conditions, there is a possibility of anionic polymerisation even under the influence of an initiating agent as weak as R_3Al.

2. Systems with Metal Alkyls and Oxygen-Containing Compounds (Quinones, Phenols, and Acyl Peroxides).

Unusual redox systems based on combinations of organometallic compounds and quinones or phenols have been studied by Furukawa et al. [17] The most notable effect was observed in the polymerisation of methyl methacrylate under the influence of $(C_2H_5)_2Cd$–quinone (or phenol) systems. The activity of such systems decreases as a function of the nature of the metal alkyl in the series $R_2Cd > > R_2Zn > R_3Al$. The formation of free radicals is attributed to reaction (16) and (17) in the case of a quinone and (18) and (19) in the case of a phenyl:



(16)

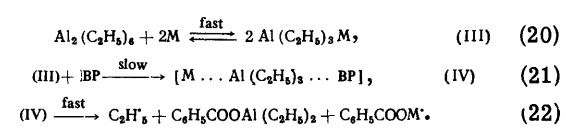
(17)

(18)

(19)

As a result of electron transfer from oxygen to cadmium, unstable addition products (I) or (II) are formed, their decomposition being accompanied by the formation of free radicals.

Milovskaya and coworkers [42–45] obtained systems comprising aluminium alkyls and acyl peroxides capable of initiating the polymerisation of polar monomers (vinyl acetate, methyl methacrylate, acrylonitrile). The process obeys the laws of free-radical polymerisation and occurs much below the temperature of the thermal decomposition of the corresponding peroxides. The step involving the formation of free radicals is unusual in this case and different from the processes occurring in organometallic compound–hydroperoxide systems. The interaction between $(C_2H_5)_3Al$ and benzoyl peroxide (BP) takes place very vigorously in the absence of the monomer by a donor–acceptor mechanism with a stoichiometric ratio of 2 : 1. Under the experimental conditions, this reaction does not stop at the stage involving the formation of the complex and results in the formation of the following final products: diethylaluminium benzoate and gaseous compounds derived from various reactions of the ethyl radical [46]. An obligatory condition for the occurrence of polymerisation is the participation of the polar monomer in the formation of an intermediate complex [42]. The sum total of the information obtained under model conditions and in polymerisation suggests that free radicals are formed in the following reactions [47]:



(III) (20)

(IV) (21)

(22)

The relation between the rate of initiation and the concentration of the components of the initiating systems obtained from Eqns.(20)–(22) leads to an expression for the variation of the overall rate of the process with the concentration of the aluminium alkyl and the peroxide, which has been confirmed experimentally:

$$V = k[M]^n[Al(C_2H_5)_3]^{1/2} \cdot [BP]^{1/2}.$$

The capacity for complex formation of monomers which are weak electron donors, such as styrene or vinyl chloride, has proved insufficient for the occurrence of polymerisation under the influence of the system $(C_2H_5)_3Al$–acyl peroxide. In this case, for polymerisation to occur, it is necessary to introduce complex-forming agents such as an ether or ester or acetonitrile[47,48]. The results of studies on the kinetics of the polymerisation of vinyl chloride with the system $(C_2H_5)_3Al$–benzoyl peroxide (BP)–ethyl acetate (EA) show that the step involving the formation of free radicals is different in this case from the corresponding reactions in the polymerisation of polar monomers. The expression for the total rate of polymerisation is

$$V = k[M]^n\left[\frac{Al(C_2H_5)_3}{\ni A}\right]^{1/4}[BP]^{1/4},$$

from which it follows that the non-complex form of the organoaluminium compound participates in the stage involving the formation of free radicals; the stoichiometric ratio of the components of the catalytic system is the same as in the model system (without monomer):

$$Al_2(C_2H_5)_6 + 2\,EA \rightleftarrows 2\,Al(C_2H_5)_3\cdot EA, \qquad (23)$$

$$2\,Al(C_2H_5)_3 + BP \xrightarrow{k_1} 2\,C_6H_5COOAl(C_2H_5)_2 + 2\,C_2H_5^{\cdot}. \qquad (24)$$

The observed difference in the behaviour of the complex-forming agents and polar monomers is evidence that the function of the latter (in the free radical formation stage) is not restricted solely to the role of complex-forming agents. Probably the displacement of the monomer by benzoyl peroxide from the complex $(C_2H_5)_3Al.M$ [reactions (21) and (22)] is accompanied by the interaction of the benzoate radical with the double bond (a reaction in the "cage"). This is reflected in a change of the stoichiometric relation between the components of the catalytic system established under model conditions[46] and in the polymerisation of polar monomers[43–45].

The fundamental difference between the mechanisms of the formation of free radicals in systems with participation of hydroperoxides and acyl peroxides is well illustrated by the dependence of the efficiency of the system on the nature of the organoaluminium compounds and monomers employed. In the formation of initiating systems based on acyl peroxides one can use only aluminium alkyls but not alkoxy-derivatives, which are weak Lewis acids and show no tendency to react with electron-donor compounds[42,44,47,49]. On the other hand, in combination with a hydroperoxide, active systems have been obtained only with mono- and dialkoxy-derivatives of aluminium and the electron-donor capacity of the monomer is not an essential condition for the process to occur[4,9,35].

The phenomenological conditions necessary for the development of the polymerisation process with participation of the system R_3Al–acyl peroxide corresponds most closely to the conditions which obtain in the polymerisation of polar monomers with modified Ziegler catalysts. Consequently systems of the first type can be regarded to some extent as models for more complex multi-component systems[50]. Razuvaev and coworkers[51] established that systems based on di-isopropylmercury and benzoyl peroxide are active initiators of the polymerisation of methyl methacrylate and vinyl chloride. The process kinetics indicate free radical polymerisation; the authors believe[52] that the formation of free radicals can probably be attributed to reactions analogous to those proposed in the study of the interaction of the above components under model conditions. The system with the organomercury compound is much less active than that obtained on the basis of aluminium alkyls.

III. SYSTEMS WITH A METAL ALKYL AND A VARIABLE-VALENCE METAL DERIVATIVE

The polymerisation of polar monomers of the vinyl series can be achieved successfully with the so called modified Ziegler catalysts. At the present time there is no single view concerning the mechanism of the process, i.e. whether they are of the radical or ionic-coordination type. Nevertheless the literature data show that there is better evidence for a radical mechanism.

In many cases the catalyst is modified by the introduction into the reaction system of a polar solvent[53–55]. Furukawa and coworkers[54,55] showed that polar monomers such as vinyl acetate or methyl methacrylate themselves behave as polar solvents. Although a rational approach to the choice of the catalytic pair does not exist, nevertheless a necessary condition for the process to occur is the separation of the catalyst components by a complex-forming agent (the monomer or solvent)[54].

Table 3. Activity of the catalytic systems metal alkyl–metal halide in the polymerisation of polar monomers* [54].

Catalyst	Monomer	t, °C	Time, h	Conversion, %
$(C_2H_5)_2Zn$–$VOCl_3$	MMA**	20	24	82
$(C_2H_5)_2Zn$–$FeCl_3$	MMA*	20	24	90
$(C_2H_5)_2Zn$–VCl_4	VA	20	24	56
$(C_2H_5)_2Cd$–VCl_4	VA***	20	27	39
$(C_4H_9)_2Hg$–$BiCl_3$	MMA	15	50	86
$(C_2H_5)_3Al$–VCl_4	VA	20	40	36

*5 ml of solvent; 2 mole % of metal alkyl; 1 mole % of metal halide; 5 ml of monomer.

**The solvent was hexane and in the remaining cases dioxan.

***3 ml of monomer and 1.5 ml of solvent.

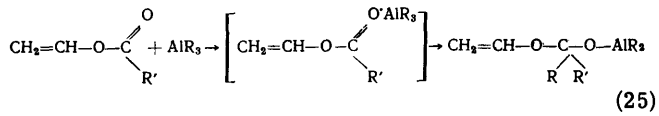
Table 3 presents certain data for the polymerisation of a number of polar monomers under the influence of systems metal alkyl–metal halides. In all cases the components are introduced in a specified order: the metal halide (MX) first, then the monomer, and finally the metal alkyl (RM).

When the order was altered, MX followed by RM and then by the monomer, polymerisation did not occur; this feature differs sharply from the behaviour of the catalytic system in the polarisation of non-polar monomers[54].

Table 4 presents data for the effect of the solvent on the activity of the catalytic system $(C_2H_5)_3Al$–VCl_4.[55]

At present it is not clear why the nature of the monomer affects the relative positions of complex-forming compounds in the activity series (Table 4). The data for the variation of the rate of the process when the order of mixing of the reacting compounds is altered in any way show that in the catalytic system $(C_2H_5)_3Al$–$VOCl_3$ both components are involved in complex formation, but the complex-forming capacities of vinyl and ethyl acetates are by no means equivalent[55]. A similar conclusion is valid also for the system $(C_2H_5)_3Al$–VCl_4 (see Table 4). It may be

supposed that this difference is associated with the irreversible consumption of part of the organoaluminium component by its interaction with the monomer:



(25)

Table 4. Effect of solvent on the activity of the system alkylaluminium–vanadium halide[55].

Monomer	Solvent	Conversion, %	Monomer	Solvent	Conversion, %
VA	n-hexane	4	MMA	n-hexane	2
	toluene	4		toluene	2
	ether	14		ether	7
	tetrahydrofuran	39		tetrahydrofuran	67
	dioxan	29		dioxan	61
	ethyl acetate	61		ethyl acetate	28
	ethanol	traces			
	acetone	traces			

Note. Experimental conditions: 5 ml of monomer, 1 mole % $(C_2H_5)_3Al$, 0.25 mole % $[VCl_4]$, 1 ml of n-hexane as solvent for the catalyst, 4 ml of solvent, room temperature, duration 24 h; order of mixing: (1) metal halide, (2) solvent, (3) monomer, (4) $(C_2H_5)_3Al$.

The occurrence of such reactions has been established for organocadmium compounds[56]. In order to elucidate the mechanism of the effect of such systems, a study was made of the copolymerisation of methyl methacrylate with styrene and of vinyl acetate with styrene using catalysts of the type RM–MX (where M in RM is cadmium, zinc, or aluminium and MX is $VOCl_3$, VCl_4, or $TiCl_4$). It was found that the composition of the copolymer is the same as in a radical process[54,57]. To confirm the radical mechanism of the polymerisation, the ESR method was also employed[54]. In the spectrum of the system ethylene dimethacrylate–$(C_2H_5)_2Zn$–$HgCl_2$ or ethylene dimethacrylate–$(C_2H_5)_2Cd$–$HgCl_2$ the same signals were observed as in the polymerisation of the same monomer under the influence of azobis(isobutyronitrile). On the basis of the data obtained, hypotheses were put forward concerning the free radical mechanism of the polymerisation of polar monomers on Ziegler catalysts[54,55,57].

One may add that in a number of studies[58,59] the possibility of the polymerisation of acrylonitrile and methyl methacrylate under conditions in which the components of the Ziegler catalyst were mixed before the addition of the monomer has been demonstrated.

The catalytic systems $(C_2H_5)_3Al$–$TiCl_4$ and $(C_2H_5)_3Al$–$Ti(OR)_4$, maintained at 0° and 30°C respectively, were used to polymerise methyl methacrylate[58,59]. In view of the enhanced content of the polymer with the syndiotactic structure (92% against 84% in the radical process), the authors concluded that non-radical polymerisation occurs in this case.

Acrylonitrile has been polymerised using the system $(C_2H_5)_3Al$–$VOCl_3$ maintained at 25°C for 20 min[60]. According to infrared spectroscopic data, the resulting polymer (M = 2325) had a structure different from that expected for a radical process.

Much attention has been devoted to the elucidation of the possible use of catalytic systems of the Ziegler–Natta type in the polymerisation of vinyl chloride. The choice of catalytic systems in this case is complicated by the fact that metal alkyls, and in particular aluminium alkyls, are capable of reacting irreversibly with the chlorine-containing monomer and the polymer[61–63]. Organoaluminium compounds are known[64–66] to take part in the reaction

$$AlR_3 + R'X \rightarrow R_2AlX + R'{-}R \qquad (26)$$

more or less readily depending on the structure of the initial compound and that of the halogeno-derivative. In many cases the process goes to completion and results in the formation of aluminium trichloride—a typical cationic catalyst. In the presence of a variable-valence metal halide, aluminium halide formed by the reaction

$$MX_n + AlR_3 \rightarrow RMX_{n-1} + R_2AlX \qquad (27)$$

reacts subsequently even more readily with the chlorine-containing component[62].

Modified catalytic systems suitable for the polymerisation of vinyl chloride differ from the classical Ziegler–Natta catalysts by the fact that they include either an organometallic compound with reduced reactivity or complex-forming agents capable of altering to some extent the nature of the catalyst components.

Table 5. Polymerisation of vinyl chloride by modified metal alkyl–metal halide catalysts[68].

Catalyst	Molar ratio triethylamine : organoaluminium component	Yield, g $TiCl_3$	$[\eta]$
iso-$C_4H_9)_2Al$ (i-C_4H_9O)–$TiCl_3$*	—	34.1	0.36
ditto	0.23	33.0	0.15
»	1.35	8.1	—
$ClAl(OC_2H_5)$ (C_2H_5) – β-$TiCl_3$*	—	11.4	0.13
ditto	0.2	26.6	0.14
$BrAl(OC_2H_5)$ (C_2H_5) – β-$TiCl_3$**	—	10.8	0.1
ditto	0.2	27.0	0.18
»	0.39	25.3	0.24
»	0.58	29.5	0.18
»	0.97	19.3	—

*Temperature 60°C, solvent—petrol.
**Temperature 60°C, solvent—benzene.

Razuvaev and coworkers[67–70] must be regarded as pioneers in the field of vinyl chloride polymerisation on complex catalysts. They employed as components of the catalytic system organic derivatives of alkoxyaluminium or an alkoxyalkylaluminium halide combined with Ti^{4+} and Ti^{3+}. The data in Table 5 show that very active catalytic systems can be obtained by a suitable choice of components.

It is interesting to note that there exists an optimum ratio of the complex-forming agent (CFA) and the organoaluminium compound, namely CFA : Al < 1, for which the yields and the molecular weights of the polymer are maximum.

It is believed[68,69] that a necessary condition for the activity of the catalytic system is the presence of an organoaluminium compound in a free state. It has been shown that in the polymerisation of vinyl chloride on modified catalysts the same rules hold as for non-polar monomers (for example, the polymeriastion of propene is influenced by electron-donor additives[71,72]). It is thought[67–70] that this is evidence of the occurrence of an ionic-coordination

process. The improved crystallinity of poly(vinyl chloride) obtained on the heterogeneous catalyst $(C_2H_5)_3Al-TiCl_3$–CFA compared with the polymer synthesised using radical initiators is quoted by the authors as confirmation of their view. However, it has been established that all poly(vinyl chloride) specimens of low molecular weight show high crystallinity regardless of the method of their preparation [73,74]. Thus the fact of improved crystallinity alone cannot be unambiguously interpreted, since the polymers obtained had $[\eta] = 0.1-0.2$.

Ashikari [75-77] investigated as catalysts for the polymerisation of vinyl chloride a number of catalytic systems of the type $(C_2H_5)_3Al-MX-MC$, where MX is the halide of a variable-valence metal (titanium, iron, vanadium, etc.) and MC is the modifying component (butanol, tetrahydrofuran, dibutyl sulphide, ethyl acetate, acetone). Fig. 3 shows the relation between the rate of polymerisation and the MC : Al ratio for the system $(C_2H_5)_3Al-VCl_3$. Depending on their effect on the rate of the process, the modifying components can be clearly divided into two groups. The first includes butanol, tetrahydrofuran, and dibutyl sulphide which give rise to a distinct maximum in terms of the variables investigated. With butanol, the maximum effect at MC : Al = 3 was attributed [75-77] to the formation of trialkoxyaluminium which is more active in the formation of the catalyst than the initial alkyl. Thus we may note that, for systems with titanium tetrachloride, dialkoxyaluminium derivatives are no longer active as co-components [68]. The maximum rate at MC : Al $\geqslant$ 1 in the presence of tetrahydrofuran or dibutyl sulphide has been explained [75-77] by the participation in the process of the complex form of the organoaluminium compound. The monotonic increase of the rate in the presence of ethyl acetate is probably associated with the formation of an alkoxy-compound:

$$R-\underset{\underset{OR}{|}}{\overset{\overset{O}{\|}}{C}} + Al(C_2H_5)_3 \rightarrow R-\underset{\underset{C_2H_5}{|}}{\overset{\overset{OAl(C_2H_5)_2}{|}}{C}}-OR \qquad (28)$$

The occurrence of this type of reaction is extremely likely, since the process was carried out at 40°C. A similar reaction can also take place in the presence of acetone which reacts in the enol form with organoaluminium compounds [78]. In this case too a monotonic increase of the rate was observed with increasing concentration of the modifying agent MC. The lack of an effect on the structure of the polymers produced and also the similarity of the copolymerisation constants of vinyl chloride and acrylonitrile to the usual constants for radical processes lead to the hypothesis of the occurrence of radical polymerisation and the influence of systems of the type $(C_2H_5)_3Al-MX-MC$. [77]

One may add to this that, on the basis of the copolymerisation constants of vinyl chloride and vinyl acetate, Baker [79] regards copolymerisation under the influence of the system $(iso-C_4H_9)_3Al-VOCl_3$ as a radical process.

Systems consisting of alkoxyaluminium compounds and various derivatives of variable-valence metals have been investigated by Giannini and Ceska [80]. The system $(C_2H_5)\cdot AlCl(OC_2H_5)$–vanadium oxide acetylacetonate proved to be the most active; vinyl chloride was polymerised down to temperatures as low as −78°C. The kinetic method was employed to elucidate the mechanism of the action of this catalyst. It was established that the variation of the reciprocal of the degree of polymerisation with the solvent : monomer ratio resembles the corresponding relation in a radical process.

On the basis of these results and the copolymerisation of constants of vinyl chloride and vinyl acetate, it was concluded that the process is of a free radical type. The authors see confirmation of this view [80] also in the fact that the structure and properties of the polymer obtained in the presence of the above catalytic systems and in radical polymerisation (at the same temperatures) are identical. When the reaction was performed under model conditions (in the absence of the monomer), the formation of gaseous compounds (ethane and butane) was observed and was attributed to the occurrence of free radical stages. The participation of ethyl radicals in the initiation step was also established by the finding that a polymer with labelled terminal groups is formed when a labelled organoaluminium component is employed (it was shown that chain transfer to aluminium does not take place). Effective catalytic systems for the polymerisation of polar monomers were obtained by Yamazaki and coworkers [81,82] using titanium tetrabutoxide in combination with organoaluminium compounds. The latter can be arranged in the following series in terms of their activity as co-components of the catalyst: $(C_2H_5)AlCl_2 \gg (C_2H_5)_2AlCl > (C_2H_5)_3Al > AlCl_3 > (C_2H_5)_2\cdot Al(OC_2H_5)$.

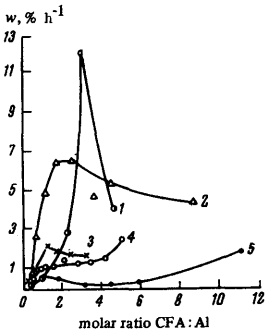


Figure 3. The effect of the nature and concentration of the complex-forming agent (CFA) on the rate of polymerisation of vinyl chloride at 40°C in the presence of the system $(C_2H_5)_3Al-VCl_3$; molar ratio Al : V = 1.37: 1) butanol; 2) tetrahydrofuran; 3) dibutyl sulphide; 4) ethyl acetate; 5) acetone.

Attention was concentrated on the polymerisation of vinyl chloride with the most active system $(C_2H_5)AlCl_2-Ti(OC_4H_9)_4$. In view of the absence of both the inhibiting effect of diphenylpicrylhydrazyl and of the effect of carbon tetrachloride as a chain-transfer agent (carbon tetrachloride did however accelerate the process) and the difference between the copolymerisation constants of styrene and vinyl chloride on the other hand and the values characteristic of radical processes on the other, it was concluded that the reaction occurring under the influence of this system (and other similar systems) is most likely to have an ionic-coordination mechanism [81,82]. For our part, we may note that many facts are fairly consistent with the hypothesis of the radical nature of the process or at least they do not contradict it. The absence of the effect of diphenylpicrylhydrazyl can be probably attributed to the higher rate of the donor–acceptor interaction ($\rangle N \rightarrow Al\langle$) than that of the reaction with participation of an unpaired electron. Furthermore, it was established that carbon tetrachloride is not a chain-transfer agent in the radical polymerisation

of vinyl chloride[83]. The interaction of organoaluminium compounds with carbon tetrachloride takes place via a free radical formation stage[84]¶, which may in fact be responsible for the acceleration of polymerisation[81,82] in the presence of carbon tetrachloride.

Budanova and Mazurek[88] made a detailed study of the kinetics of the polymerisation of vinyl chloride with $Ti(OC_4H_9)_4$–(iso-$C_4H_9)_2AlCl$, which is very similar to those discussed above[81,82]. They established that the dependence of the rate of polymerisation on the concentration of the components of the initiating system and the rate of formation of Ti^{3+} under model conditions are consistent with a typical radical reaction with bimolecular chain termination. The variation of the reciprocal of the degree of polymerisation with the rate of the process is characteristic of free-radical initiation. The ratio k_{term}/k^2_{prop} obtained proved to be equal to the value quoted for radical initiation[89].

One of the proofs for the ionic-coordination polymerisation of vinyl chloride on modified Ziegler catalysts is the possibility of copolymerising it with propene[82,90]. However, Imoto and coworkers[91] established that vinyl chloride copolymerises with propene also under the influence of radical initiators [azobis(isobutyronitrile)]; as a result, the very fact of the formation of the copolymer in the system metal alkyl–metal halide cannot be interpreted unambiguously. One could postulate that in the case of modified Ziegler catalysts two processes take place: one, with an ionic-coordination mechanism, leads to the formation of polypropylene and the other has a radical mechanism involving the participation of vinyl chloride. The formation of the copolymer may be regarded as a result of the generation of a radical centre in the main chain of the polypropylene, which then initiates the grafting of vinyl chloride or recombines with the growing poly(vinyl chloride) radical.

The results of studies of the polymerisation of polar monomers with many modified catalysts show that the concept of the development of a radical process is in this case fairly well founded[54,55,57,77,79,80,88].

We shall now examine the problem of what reactions between the components of the Ziegler catalyst lead to the formation of free radicals. Unfortunately there are almost no literature data on the interaction between the components of the initiating systems effective in the polymerisation of polar monomers; systems which are relatively inactive in such processes have been mainly examined. Therefore the information given below is to some extent arbitrary.

The reactions between organoaluminium compounds and titanium derivatives have been studied in a number of investigations[92–104]. The rate of reaction and the degree of reduction of titanium depend on the nature of the reacting compound: for example, the interaction of triethylaluminium with titanium tetrachloride at a moderate temperature takes place rapidly even in dilute solution[97]. When the concentrations of R_3Al and $TiCl_4$ are approximately equal, then, on the basis of the final products, the reaction between them can be described as follows:

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + RTiCl_3 \downarrow \quad \frac{1}{2}RH + \frac{1}{2}R_{-H} + TiCl_3. \qquad (29)$$

The formation of gaseous compounds (methane, ethane, and butane when R = methyl or ethyl) has been attributed to the breakdown of the organotitanium derivative into free radicals with subsequent reactions of the latter[92–96]. A series of alkyl derivatives of titanium have been obtained and investigated†. They are thermally unstable, the most stable being the methyl derivative. Ethyltitanium trichloride decomposes in 24 h at 20 °C.[106]

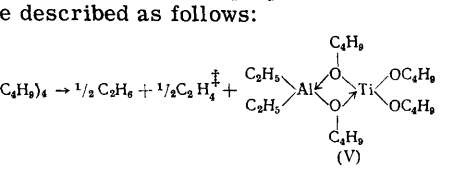
The interaction of CH_3TiCl_3 with carbon tetrachloride in the presence of metallic mercury takes place via intermediate stages in which free radicals take part[107]. The possibility of the radical polymerisation of vinyl chloride under the influence of organotitanium compounds in combination with carbon tetrachloride has been established[108].

North[109] showed that the polymerisation of styrene under the influence of $RTi(OC_3H_7)_3$ obeys the laws governing free radical reactions. A number of investigators, however, believe that the breakdown of organotitanium compounds takes place without the formation of free radicals and is subject to relations characteristic of bimolecular reactions[98–104]. On the basis of a study of the products of the reaction of $TiCl_4$ with $(C_2H_5)_2AlCl$, de Vries[99] concluded that in this case free radicals are not formed. This conclusion has been confirmed by experimental facts: when the reaction is carried in cumene, dicumenyl (the product of the recombination of the radicals formed when hydrogen is removed from cumene) was not observed; in the reaction in a deuteriated solvent, deuterium was not detected in the gaseous product. On the other hand, the interaction with a deuteriated aluminium alkyl leads to gaseous products which contain an amount of deuterium consistent with the initial content. The formation of such gaseous compounds has been explained[99] from the standpoint of the "self-consistent" bimolecular interaction in which a β-hydrogen atom is transferred from one molecule of the organotitanium compound to another:

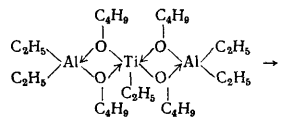
$$2\,TiCl_3{-}CH_2{-}CH_3 \rightarrow 2\,TiCl_3 + C_2H_6 + C_2H_4. \qquad (30)$$

De Vries[99] noted that such concepts are particularly useful for the understanding of the stability of methyl derivatives. Shilov and coworkers[102] established that the interaction of $Ti(OR)_4$ with $(C_2H_5)_3Al$ is a two-stage process: initially there is a rapid reaction with evolution of ethane, whose amount corresponds approximately to half of the initial $Ti(OR)_4$ [reaction (31)] and then ethane is formed slowly as a result of reaction (32), which takes place subsequently. When the above reactants interact in deuteriotoluene, deuteriated ethane is not detected in either the first or the second portions of the gas. According to the authors[102], these findings indicate the absence of free radical stages and the formation of gaseous products is a consequence of intramolecular disproportionation. The process can be described as follows:

$$Al(C_2H_5)_3 + Ti(OC_4H_9)_4 \rightarrow {}^1/_2\,C_2H_6 + {}^1/_2C_2H_4^{\ddagger} + \text{(V)} \qquad (31)$$



$$V + Al(C_2H_5)_3 \rightarrow \text{(VI)} \rightarrow \text{slow decomposition}. \qquad (32)$$

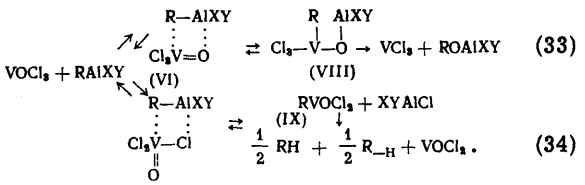


¶ Systems of the type aluminium alkyl–carbon tetrachloride have been used to initiate the polymerisation of vinyl chloride[85–87].

† See the review of Razuvaev and Latyaeva[105].

‡ The absence of ethylene from the gas evolved is explained by its possible polymerisation.

In the study of the kinetics of the decomposition of CH_3TiCl_3 in carbon tetrachloride Beerman and Bestian[110] established that in this case there is a bimolecular reaction; less than 1% of methyl chloride was detected in the reaction products, which is evidence of only insignificant participation of free radicals in the process. The interaction of organoaluminium compounds with vanadium derivatives, in particular with $VOCl_3$ has been little studied. Petrov showed[111] that the rate of reaction of $VOCl_3$ with $(C_2H_5)_3Al$ is very high; at room temperature the reduction process terminates after less than 2–3 min. Since two possible pathways exist, the process is much more complex than with titanium tetrachloride:



(33)

(34)

The rate of reaction by a particular pathway depends on the relative likelihood of the formation of intermediate complexes (VI) and (VII) and on the stability of compounds (VIII) and (IX).[111] In recent years reliable proof of the formation of organovanadium compounds has been published§. In the study of the mechanism of the breakdown of phenylvanadium oxide dichloride[112] it was established that the decomposition kinetics indicate the occurrence of the following monomolecular reaction:

$$C_6H_5VOCl_2 \rightarrow [C_6H_5^{\cdot} + VOCl_2] \rightarrow C_6H_5{-}C_6H_5. \qquad (35)$$

However, the hypothesis of a radical mechanism for this process is inconsistent with the absence of other reactions characteristic of a highly active phenyl radical (for example the products of the reaction with the cyanodimethylmethyl radical have not been detected, there is no interaction with carbon monoxide, etc.).

Another mechanism has been suggested for the formation of biphenyl[112], which is also consistent with monomolecular decomposition kinetics:

$$2\,C_6H_5VOCl_2 \rightleftarrows (C_6H_5)_2VOCl + VOCl_2, \qquad (36)$$

$$(C_6H_5)_2VOCl \xrightarrow{k} C_6H_5{-}C_6H_5 + VOCl. \qquad (37)$$

The rate of formation of biphenyl is

$$V = k[(C_6H_5)_2VOCl].$$

The equilibrium constant corresponding to reaction (36) is

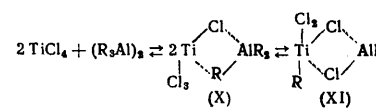
$$K = \frac{[(C_6H_5)_2VOCl]^2}{[(C_6H_5)_2VOCl_2]^2}$$

whence

$$V = k \cdot K^{1/2}[C_6H_5VOCl_2]$$

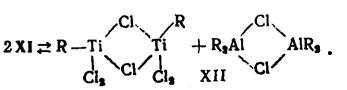
The data quoted demonstrate that the usual procedures in many cases failed to detect the formation of free radicals in the reaction between the components of a Ziegler system in non-polar media. Comparison of the kinetic data for the polymerisation of vinyl chloride under the influence of $(iso\text{-}C_4H_9)_2AlCl{-}Ti(OC_4H_9)_4$ and for the interaction of these components under model conditions established that the fraction of free radical reactions amounts to about 1%.[88] The explanation of the impossibility of isolating the reaction products of free radicals, in particular in experiments with deuteriated solvents, should be based on this finding in the first place. Thus the most sensitive indication of the reactions between the components of the catalyst is the polymerisation itself.

We shall now attempt to represent more fully the reactions which may occur in the catalytic system and the role of the complex-forming agents in the process in those cases where they do not lead to the irreversible consumption of the organometallic compound (the function of the polar monomer should also be determined mainly by its capacity for complex formation). Organoaluminium compounds, which are electron deficient, are known to be capable of forming dimeric species and to participate readily in radical exchange reactions[113–115]. It may be supposed that the first stage of the reaction with a variable-valence metal is the formation of the following association complexes[97]:



(38)

The bimolecular decomposition of compound (XI) leads to the gaseous compounds R–R and $RH(R_{-H})$. Another reaction pathway for the association complex (XI) may be a bimolecular rearrangement of the type¶



(39)

The formation of free radicals may be attributed to the monomolecular decomposition of the organotitanium complex (XII). However, in view of the similarity of the radicals formed, this process takes place mainly by a cryptoradical mechanism with a very small amout of free radicals liberated in the reaction space. The preferential course of the reaction towards the formation of the complexes (XI) or (XII) is associated with the structure of the initial compounds. The specificity of the components of the Ziegler system capable of effecting radical polymerisation consists in the fact that the interaction between them leads to the formation of species tending to undergo homolytic breakdown. In this connection we may note that the stability of organotitanium compounds depends on the nature of R and X (in compounds of the type R_nTiX_{4-n}) and lies in the order indenyl > α-naphthyl > phenyl > *p*-anisyl > > ethynyl > methyl > butyl. On the other hand, the stability increases when the group X has the optimum electronegativity, which is not as high as in the case of fluorine and not as low as in the case of an alkoxy-group[116,117].

The role of complex-forming agents reduces in the first place to the retardation of the subsequent interaction of the metal alkyl and the variable-valence metal having made good their electron deficit; as a result there is a possibility of radical generation in the course of time from rapidly reacting components. The question of the further interaction between the catalyst components in the presence of the complex-forming agent, i.e. the question of the driving forces for this process, remains insufficiently clear. Two pathways may be postulated: in one of them the reaction takes place via non-complex species through the following equilibria:

$$MR_n + K \rightleftarrows MR_n \cdot K,$$
$$MX + K \rightleftarrows MX \cdot K. \qquad (40)$$

§ See the review of Razuvaev and Latyaeva[105].

¶ The absence of an ESR signal in the study of precipitates containing trivalent titanium suggested the existence of dimeric species in titanium halides[100].

i.e. the function of the complex-forming compound is to decrease the concentration of the reacting compounds. This course of the process has been established in the study of the kinetics of the reaction of $(iso\text{-}C_4H_9)_2AlCl-Ti(OC_4H_9)_4$ in the presence of ethyl acetate[118]. Another possibility is the reaction of the complex with displacement of one electron-donor compound by another[119], for example:

$$K\cdot AlR_3 + MX \rightarrow [K \ldots AlR_3 \ldots MX] \rightarrow K + AlR_3\cdot MX\,. \qquad (41)$$

The existence of pentacoordinate aluminium has been unambiguously established recently on the basis of isolated and characterised complexes having the composition

$(C_2H_5)_2AlI\cdot 2\,C_5H_5N$[120] and $(C_2H_5)_3Al\cdot 2,2'$-dipyridyl.[121]

These reactions do not exhaust the role of complex-forming compounds. Association complexes formed by reactions (38) and (39) are also acted upon by the polar reagent, particularly the complexes containing titanium alone [compound (XII)]. There are grounds for the belief that in this case cryptoradical reactions are transformed into true radical reactions. Beerman and Bestian[110] showed that, when CH_3TiCl_3 is decomposed in ether, the process kinetics and the nature of the products formed change. The rate of decomposition increases enormously and the variation with time is consistent with a monomolecular and not a bimolecular reaction. The authors attribute the observed phenomenon to the loosening of the TiR bond under these conditions, which ultimately leads to its homolytic dissociation; the yield of ethane is 28%, while in the absence of ether its amount is negligible.

The decomposition of $C_5H_5VOCl_2$ in the presence of tetrahydrofuran, acetonitrile, and butyl ether is treated by Shilov and coworkers[122] as a free radical process occurring as a result of the increase in the degree of specific solvation of $VOCl_2$ formed relative to the initial compound. A detailed study of the kinetics of the reaction of $(iso\text{-}C_4H_9)_2AlCl$ with $Ti(OC_4H_9)_4$ in the presence of ethyl acetate was made by Budanova and Mazurek[118], who showed that the role of the complex-forming agent at concentrations higher than that of the organoaluminium compound is not restricted solely to the interaction with the initial metal alkyl. In this case there is a change in the order of the reaction with respect to the components of the initiating system, corresponding to a transition from bimolecular to monomolecular breakdown of the intermediate complex of the alkyl derivative of titanium(IV) with generation of free radicals.

The above hypotheses concerning the chemistry of the formation of free radicals and the role of complex-forming compounds are to a large extent tentative. Nevertheless they make it possible to understand the causes of the difference between ionic-coordination polymerisation and the polymerisation of polar monomers. The latter gives rise not to the final reaction product MR_n-MX_m but to unstable intermediate compounds formed in the course of this reaction.

At the present time the hypothesis that in ionic-coordination polymerisation the propagation steps are preceded by the coordination of the double bond of the monomer to the unfilled orbitals of the variable valence metal has been widely adopted. As shown for titanium tetrachloride, in the case of polar monomers where the heteroatom is in the β-position with respect to the double bond the preferred coordination site is located at the polar groups[123]. To what extent such concepts are valid also for trivalent titanium (or other metals in a lower valence state) remains obscure at present. Therefore we should note that the literature data quoted, indicating the occurrence of radical polymerisation of polar monomers using Ziegler catalysts, nevertheless do not exclude the possibility that in special cases ionic-coordination polymerisation of this class of monomers can also take place.

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During the preparation of the manuscript for the press new literature data were published which can usefully supplement the corresponding sections of the review.

1. The problem of whether the conversion of organic peroxoboron derivatives into alkoxyboron derivatives takes place by an intramolecular or intermolecular mechanism[22-27] was examined in detail by Mirviss[124].

2. It is interesting to compare the postulates put forward by Hansen[34] with the results of Bednarec et al.[125], who investigated the polymerisation of vinyl chloride under the influence of $(C_4H_9)_3B-O_2$ and showed that the overall activation energy for the polymerisation reaction varies from 11 to 6.5 kcal mole^{-1} between 0° and −30°C and between −40° and −70°C respectively. According to Bednarec et al.[125], the observed effect is evidence for the coexistence under such conditions of several types of initiating systems, which leads to the variation of the activation energy for the initiating reaction and correspondingly the overall energy of the process.

3. It has been established[126] that the interaction of $AlPh_3$ with benzophenone under model conditions is accompanied by the formation of free radicals. This is associated with the ease of homolysis of the adduct $(Ph_3COAlPh_2)_2$ and not with one-electron transfer, postulated[17] for organocadmium compounds.

4. We believe it to be appropriate also to quote data for a very interesting system obtained by combining an aluminium alkyl with azobis(isobutyronitrile)[127]† and to compare the results with other data[42-48]. It has been shown[127] that the systems investigated [R_3Al–azobis(isobutyronitrile) or R_2AlCl–azobis(isobutyronitrile)] are capable of initiating the radical polymerisation of vinyl chloride and styrene (but not methyl methacrylate) at a lower temperature than is the case in the breakdown of the azobis(isobutyronitrile) itself. The nature of the radicals identified by electron spin resonance (ethyl and cyanodimethylmethyl) indicates the participation of both components of the system in the generation of free radicals. The authors[127] attribute their findings to the formation of the complex R_3Al–azobis(isobutyronitrile) (via the nitrile group of the latter) in which radical breakdown is facilitated.

5. The data quoted in Refs. 58 and 59 and 128 are supplemented by the findings that the polymerisation of methyl methacrylate by the catalytic system $(C_2H_5)_3Al-Ti(OC_4H_9)_4$ is also regarded as a catalytic process.

6. In the course of further development of their studies[81,82], Yamazaki and coworkers[129] investigated the polymerisation of deuteriated vinyl chloride by the system $(C_2H_5)AlCl_2-Ti(OR)_4$ and established the presence of terminal alkyl groups. This suggested that the initiation process may have a radical mechanism. However, the authors believe that the nature of the propagation stage is still obscure.

7. The work of Ulbricht et al.[130], who concluded that the polymerisation of vinyl chloride under the action of the

† This is the first piece of evidence indicating the possibility of influencing catalytically the rate of decomposition of azobis(isobutyronitrile).

system $TiCl_4$–Et_2AlOEt–dioxan (on the basis of their kinetics and the measured copolymerisation constants for vinyl chloride–styrene), is related to the investigation in Refs. 80 and 88.

8. The concepts put forward in Refs. 82, 90, and 91 may ber supplemented by the results of Yamazaki and Aridomi[131], who showed that, depending on the composition of the catalyst $TiCl_x(OC_4H_9)_{4-x}$–$AlCl_y(C_2H_5)_{3-y}$ (where x = 0–4 and y = 0–2), the vinyl chloride–propene copolymerisation constants may correspond to either a radical or an ionic-coordination process. Yamazaki and Aridomi[131] suggest that this finding should be attributed to the possibility of the polymerisation of vinyl chloride itself by one or other mechanism.

9. In agreement with the results of Beerman and Bestian[110], it has been shown[132] that the breakdown of CH_3TiCl_3 in tetrahydrofuran is homolytic. The formation of the CH_3 radical has been confirmed by the presence in the reaction mixture of CH_3D when the reaction is carried out in deuteriotoluene.

10. It is interesting to compare the effect of complex-forming additives on the type of decomposition of variable-valence organometallic compounds, established under model conditions[110,122,132], with the findings for the polymerisation process. Thus it has been shown[133] that in the copolymerisation of ethylene with vinyl chloride by the catalytic system Et_2AlCl–$Ti(OR)_4$ the addition of electron donors (tetrahydrofuran, pyridine, ethyl ether, diethylamine) leads to the formation of copolymers, the structure of which fully corresponds to that obtained under the conditions of a radical process[134].

11. A fundamentally new procedure for the ionic-coordination polymerisation of polar monomers by Ziegler catalysts was proposed by Giannini et al.[135] Its essential feature is that one uses in the reaction either monomers with sterically hindered (with respect to the reactions with the catalyst) functional groups or monomers with reduced electron-donor capacity (this is achieved by preliminary complex formation with an organometallic compound or by using monomers containing O–Si bonds).

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