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ORGANOMETALLIC COMPLEXES — OLEFINE POLYMERISATION CATALYSTS

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After the discovery by Ziegler of a new method of synthesising polyethylene, complex organometallic catalysts came to be widely used in macromolecular chemistry.

The most important act in the intricate process of polymerisation, using organometallic complex catalysts, is the formation of the complex. The different aspects of the mechanism of the formation, and the catalytic action of organometallic complexes, have been widely discussed in the literature, including this journal[1]. However, recent work necessitates a reassessment of the concepts regarding the nature of the activity of organometallic catalysts in the polymerisation of unsaturated hydrocarbons.

1. METALALKYLS — OLEFINE POLYMERISATION CATALYSTS

Certain simple organometallic compounds act catalytically in the polymerisation of ethylene, even in a homogeneous phase[2]. However, by no means all partially ionic compounds with a metal–hydrocarbon bond possess such catalytic properties. Thus, the typically ionic alkyls of the alkali metals (sodium to caesium) are not α-olefine polymerisation catalysts and are found to be active only in the polymerisation of diolefines. Organometallic compounds of the alkali-earth metals (calcium to barium) likewise do not display catalytic activity in the polymerisation of ethylene. But aluminiumalkyls (ionic character of the bond 22%) and lithiumalkyls (43%) polymerise ethylene to low-molecular polymers, and give dimers with other α-olefines.

It is evident from a comparison of the behaviour of a few simple metalalkyls that the strongest catalytic action in the polymerisation of ethylene is shown by the alkyls of metals which have the smallest ionic diameters (Li, Be, Al; see Table 1). These metals belong to the first subgroups of the first three groups of the periodic classification and very easily form complexes. However, boron, which also has a very small ionic diameter, forms organometallic compounds which have the lowest catalytic activity. This is explained by the low electropositivity of the metal (2.0 eV on Pauling's scale of electronegativity). Therefore, the most active polymerisation catalysts are the organometallic compounds of strongly electropositive metals with small ionic diameters[3].

Lithiumalkyls are present as dimers in hydrocarbon solvents and are catalysts for the stereospecific polymerisation of isoprene[4], the polymer, formed by catalysis, having the 1,4-*cis*-configuration. In ether solution lithiumalkyl loses its stereospecific effect and forms an atactic polymer by 1,2-combination of monomeric units. The most likely reason for stereospecific 1,4-*cis*-polymerisation is obviously the small $Li^+(CH_2)^-$ spacing and the ability of lithium to form complexes:

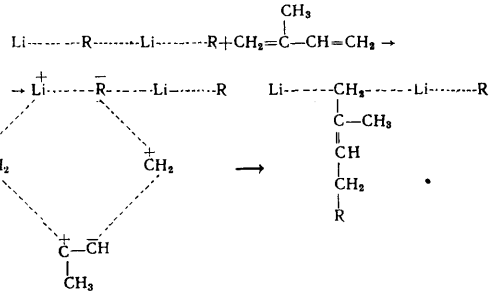
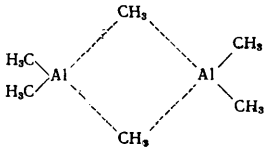


TABLE 1.

Metal	Electronegativity according to Pauling, eV	Atomic radius, Å	Ionic radius, Å	Metal	Electronegativity according to Pauling, eV	Atomic radius, Å	Ionic radius, Å
Li	1.0	1.33	0.68	Zn	1.5	1.31	0.74
Na	0.9	1.57	0.97	Ca	1.0	1.74	0.99
K	0.8	2.03	1.33	Ba	0.9	1.98	1.34
Rb	0.7	2.16	1.47	B	2.0	0.88	0.23
Cs	0.8	2.35	1.67	Al	1.5	1.26	0.51
Be	1.5	0.90	0.35	Si	1.8	1.17	0.42
Mg	1.2	1.36	0.66				

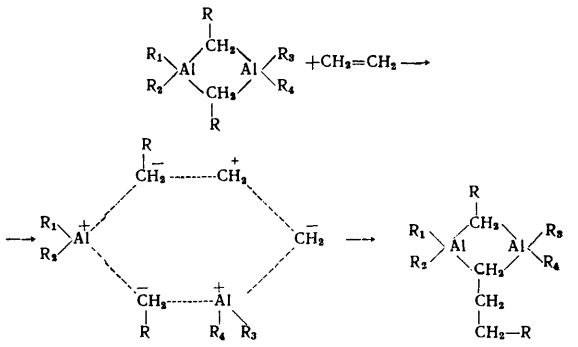
Note. Underlined metals are strongly electropositive and have small ionic radii.

Alkyls of aluminium and beryllium also tend to form complexes. This is confirmed by the fact that they are usually found in dimeric form. By electron-diffraction and X-ray analysis of trimethylaluminium dimer, the C–Al spacing was calculated for both carbon atoms forming the bridge between the two Al atoms, and found to be equal to 2.24 Å, which is far greater than the C–Al spacing in the four terminal bonds (1.99 Å). This is the reason for the much easier dissociation of the bridge bonds.



In this compound the univalent CH_3 group with one unpaired electron is joined to two atoms of aluminium. A tricentric orbital is thus formed, with two electrons revolving in the field of three nuclei. Such a "tricentric" bond has an energy about 10 kcal higher than that of the usual Al–CH_3 bond[5]. This feature of aluminium, beryllium, and certain other elements is connected with the fact that the valency of atoms is specified not only by the number of unpaired electrons which an atom can use for the formation of chemical bonds, but also by the presence of unfilled orbitals. Thus, although an aluminium atom has only three electrons available for bond formation, it can supply four orbitals. Therefore, despite the deficiency of electrons, the formation of tricentric orbitals provides sufficiently stable bonding.

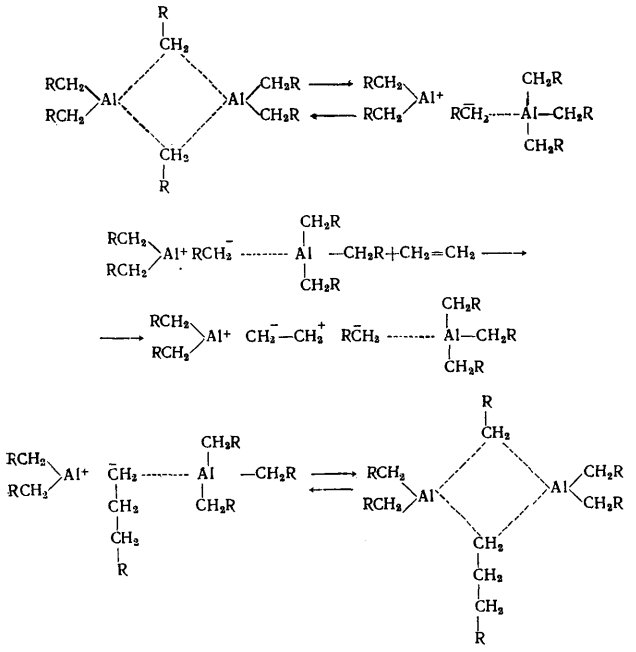
It is characteristic that in molecules of this type the angle between the bonds formed by the carbon atoms and the two metals atoms is equal to 60°–70°, since the two metal orbitals combine with the tetrahedral orbital of the CH_3 carbon. As a result, the two Al atoms are brought closer together. This is hindered if the radius of the metal atom is large. Natta[2] explains the catalytic action of the simple organometallic compounds in the polymerisation of ethylene in terms of the coordination of the electron-rich carbanion (formed by the polarisation of the ethylene molecule, $CH_2=CH_2 \rightarrow {}^-CH_2-CH_2^+$) to the electron-deficient complex. This is accompanied by the dissociation of the bridge metal–alkyl bond:



The solubility of ethylene in heptane and its heat of solution are not increased in the presence of R_3Al, which means that addition of ethylene molecules (by means of their p electrons) to the electron-deficient aluminium molecule does not take place with a low activation energy.

In a consideration of the various interpretations of the mechanism of ethylene addition, the electrical conductivity of R_3Al solutions in hydrocarbons cannot be disregarded. Bonitz[6] ascribed this conductivity to ionic dissociation.

When a polarised ethylene molecule is placed between two oppositely charged ions we have:



Even the most active of the simple metal alkyls considered above (alkyls of Al, Be, Li) polymerise ethylene rather slowly by successive (gradual) addition and allow only low-molecular polyethylene to be obtained (average molecular weight below 10 000). The reason for this is probably that at the elevated temperatures at which this reaction takes place (120°–250°), the chain-breaking reaction is very rapid; moreover, when the chain becomes very long, the polymer has a tendency to crystallise, thus blocking the small metal atoms firmly bound to the end of the chain.

2. THE ROLE OF ORGANOTITANIUM COMPOUNDS IN OLEFINE POLYMERISATION

The high catalytic activity of organotitanium compounds in the polymerisation of α-olefines has been demonstrated experimentally. As early as 1956 it was suggested that organotitanium compounds might act as catalysts in the polymerisation of ethylene and propene[7]. Recent work has shown[8] that organotitanium compounds — $RTiCl_3$ and R_2TiCl_2 — which are active catalysts in the polymerisation of α-olefines, can be isolated from mixtures of $TiCl_4$ and aluminiumalkyls. As the equilibrium position is unfavourable[9], special complex-forming compounds must be added to drive the reaction in the required direction. Sodium chloride or diphenyl oxide are used as additives. Methyltitanium trichloride consists of dark-violet crystals, melting at 28°–29° to a yellow liquid. The boiling point, from extrapolation of the vapour pressure curve, lies at about 120°. Other organotitanium compounds ($C_2H_5TiCl_3$ and iso-$C_4H_9TiCl_3$), which are less stable than the methyl derivative, were obtained in the same way.

The author of this work considers that in the polymerisation of ethylene with organotitanium catalysts a monomer molecule is inserted in the Ti–C bond, resulting in the formation of high-molecular organotitanium compounds. This was demonstrated experimentally by allowing the polymers to react with deuterated water or deuterated alcohol, when a deuterated hydrocarbon separated:

$$CH_3(CH_2-CH_2)_n.TiCl_3 + ROD \rightarrow \rightarrow CH_3(CH_2-CH_2)_nD + ROTiCl_3.$$

Spectroscopic examination of the polymer in the infra-red absorption region showed that unsaturated groups were present:

$$CH_2=CH_2, \quad -CH=CH-, \quad \text{and} \quad \rangle C=CH_2.$$

These may be formed by decomposition of the organotitanium compound, for example, as follows:

$$RCH_2-CH_2-TiCl_3 + CH_3TiCl_3 \rightarrow \rightarrow 2TiCl_3 + RCH=CH_2 + CH_4.$$

In the polymerisation of ethylene with the catalyst $RTiCl_3$ + + $TiCl_3$ ($TiCl_3$ is formed in the partial decomposition of $RTiCl_3$) comparatively low-molecular polymers were obtained (η_x = 0.4–1.0).

At present there is every reason to believe that organotitanium compounds play an essential part in the common Ziegler catalysts, as Ziegler admits[10]. This may explain the previously established effect of aging of the $TiCl_4$ + + R_3Al complex catalysts, *i.e.* the unstable organotitanium compounds have time to decompose and the catalyst activity is sharply reduced. In order that the catalyst may retain its activity, conditions for the continuous formation of organotitanium compounds are required. One successful practical method of accomplishing this is the gradual addition of R_3Al to the $TiCl_4$ in the reaction medium[11]. The activity of the catalyst complex is also preserved by introducing a small amount of oxygen with the ethylene to be polymerised. It has been shown experimentally[12], that there is a definite optimum oxygen content of the ethylene, at which the yield of polymer is substantially higher. This effect was studied by the present authors in the polymerisation of propene[13].

Especially interesting are the experimental data[8] showing that small amounts of oxygen first of all oxidise $TiCl_3$ to $TiCl_4$, despite the presence of R_3Al in the system. Subsequently $TiCl_4$ is again alkylated by R_3Al. Thus the reactivity of the organotitanium compound is continuously regenerated and the high activity of the catalyst complex is maintained.

It is also reported[14] that the most likely active centres of polymerisation are the organotitanium compounds. The formation of the catalyst is obviously least complicated when LiR and $TiCl_4$ are used. This reaction can be represented by the following equation:

$$TiCl_4 + nLiR \rightarrow nLiCl + TiCl_{4-n}R_n,$$

where n = 1, 2, 3, or 4. Ludlum *et al.*[14] suppose that ultimately the organotitanium compound breaks down by a free-radical mechanism with the formation of RTiCl, which appears to be an active form of the catalyst. However, this idea is not supported by experiment and for the present can only be considered as a conjecture.

Study of the change in the activity of the catalyst complex with time showed that the gradual decrease in activity in the course of polymerisation is caused by the active catalytic centres becoming blocked by the adsorbed polymer which is insoluble in the reaction medium. If the polymerisation is conducted under conditions such that a soluble polymer is formed (low molecular weight), then decrease in the rate of polymerisation does not occur.

The data on the application of certain other titanium compounds[15], in particular $C_6H_5Ti(iso\text{-}C_3H_7O)_3$, in the catalytic polymerisation of propene are interesting from a theoretical point of view. In this case only low-molecular oil is formed. The organotitanium compound $TiCl(OC_2H_5)_3$ has higher catalytic activity than the compound which does not contain chlorine but here too there was considerably less polymerisation of propene than when $TiCl_4$ was used.

The $Ti(iso\text{-}C_3H_7O)_4 + TiCl_4$ catalyst system has a high activity in the polymerisation of propene yielding liquid polymers (yield 93–96%). Razuvaev *et al.*[16] have shown that the best results are obtained with a (three–six) fold excess of $TiCl_4$. Unfortunately the results of the polymerisation of propene with pure $TiCl_4$ are not quoted, although it has been known for a long time that $AlCl_3$, $TiCl_4$, and other similar substances can catalyse the polymerisation of propene, yielding low-molecular viscous products.

It has been shown that a very rapid exchange reaction takes place between $TiCl_4$ and $Ti(OR)_4$ with the formation of compounds of the type $TiCl_n(OR)_{4-n}$, where $n = 1-3$;[17] n depends on the molar ratio of $TiCl_4$ and $Ti(OR)_4$. In the present case the reaction

$$3TiCl_4 + Ti(OR)_4 \rightarrow 4TiCl_3OR$$

takes place.

It is believed that the organo titanium compound formed is the catalyst in the polymerisation of propene. It is curious that freshly-prepared catalysts, consisting of the specially synthesised compounds $TiCl_3(iso\text{-}C_3H_7O)$, etc. have low initial activity, which increases on storage. This is accompanied by decomposition with the separation of liquid and gaseous products which were shown to consist of HCl and the corresponding alkyl chlorides. The solid decomposition product is titanium oxychloride, which is obviously responsible for the activity of the catalyst system in propene polymerisation.

3. ORGANOBIMETALLIC COMPLEXES

According to recently published data[18], a necessary condition for the formation of an active catalyst of high-molecular polymerisation of ethylene is the presence of three components in the catalyst system: an alkyl donor, quadrivalent titanium, and an electrophilic reagent. The alkyl donor can be any metalalkyl or its derivative (for example, the hydrides of lithium, aluminium, zinc, tin, and many other metals). Quadrivalent titanium may be represented as $TiCl_4$, $Ti(OR)_4$, or $(C_2H_5)_2TiCl_2$. The electrophilic reagent may be $AlCl_3$, R_2AlCl, $SbCl_5$, etc.

In the polymerisation systems commonly used the necessary electrophilic reagent is formed by reaction between R_3Al and $TiCl_4$:

$$R_3Al + TiCl_4 \rightarrow R_2AlCl + RTiCl_3.$$

In a study of various metalalkyls, Roha *et al.*[18] noted that $Sn(C_4H_9)_4$, for example, does not have a marked ability to reduce $TiCl_4$, but is a good alkyl donor and forms a catalyst of high activity by interaction with $TiCl_4$ in conjunction with the electrophilic $AlCl_3$. This confirms the need for three components to be present in the catalytic systems, including an electrophilic reagent.

A very curious fact is the observation made by the authors[13] regarding the absence of reduction of $TiCl_4$ in their catalytic system. In spite of this the catalyst promoted rapid polymerisation of ethylene to high-molecular polyethylene. Similar observations were made in the investigation of $(iso\text{-}C_4H_9)_2AlCl$. This compound has a very low reducing power but is nevertheless a good alkyl-donor and electrophilic reagent. Here also, on interaction with $TiCl_4$, an active ethylene polymerisation catalyst was formed, which allowed the reaction to be conducted at a steady, easily controlled rate. It is possible that the active catalyst is an organotitanium compound which is formed, but this was not confirmed.

The polymerisation reaction with the usual Ziegler catalyst begins rapidly, but before long the rate falls as reduction of titanium by excess metal alkyl absorbs the necessary Ti^{4+}. Slow continuous addition of an oxidising agent such as O_2,[12] ensures the presence of a sufficient quantity of Ti^{4+} and therefore activates the "dying" catalyst.

Table 2 presents experimental data obtained in the polymerisation of ethylene (in benzene at 50°–60°) with various catalyst systems. The data confirm the idea regarding the three components which are necessary to endow the organometallic complexes with high catalytic activity.

According to the data in Table 2, the character of the alkyl-donor has considerable importance; for example, $(iso\text{-}C_4H_9)AlCl_2$ being a weak alkyl-donor, although also a good electrophilic reagent, does not form an active catalyst complex with $TiCl_4$. On the other hand, a good alkyl donor, such as di-isobutylaluminium acetylacetonate, by itself, also does not form an active catalyst with $TiCl_4$ since it is not electrophilic in character; in combination with enough electrophilic $(iso\text{-}C_4H_9)AlCl_2$ an active catalytic complex is obtained.

Unfortunately the data does not include quantitative characteristics of the catalysts investigated; even the molecular weight and other elementary properties of the polyethylene obtained are not quoted. This eliminates any possibility of estimating with sufficient reliability the activity of the catalysts from the polymerisation rate constant. It should be mentioned that the experimental data discussed above contradict earlier communications[19–25]

TABLE 2. Comparison of the activities of various organometallic catalysts in the polymerisation of ethylene.

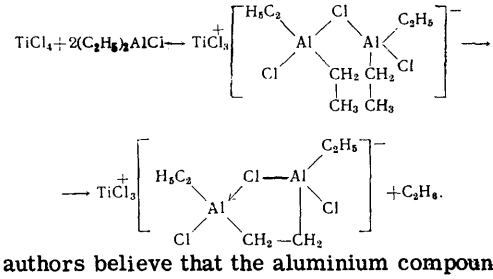
Alkyl-donor		Electrophilic agent		$TiCl_4$, mmoles	Activity in ethylene polymerisation
mmoles	compound	mmoles	compound		
12	$(iso\text{-}C_4H_9)_3Al$*	—	—	15.0	very poor
12	»	7.5	$AlCl_3$	15.0	good
5.5	95% $(iso\text{-}C_4H_9)_3Al$ + + 5% $(iso\text{-}C_4H_9)_2HAl$	—	—	11.0	good
5.5	89% $(iso\text{-}C_4H_9)_3Al$ + + 11% $(iso\text{-}C_4H_9)_2Al$	—	—	11.0	good
	ditto	5.5	$(iso\text{-}C_4H_9)_2AlCl$	11.0	very good
	»	8.25	»	8.25	very good
	»	8.00	»	3.0	good
11.0	63% $(iso\text{-}C_4H_9)_3Al$ + + 34% $(iso\text{-}C_4H_9)_2Al$ + + 3% $(iso\text{-}C_4H_9)_2HAl$	—	—	11.0	good
		11.0	$(iso\text{-}C_4H_9)AlCl_2$	11 0	very poor
5.5	Aluminiumdi-isobutyl acetylacetonate	—	—	11.0	very poor
5.5	ditto	2.0	$(iso\text{-}C_4H_9)AlCl_2$	11.0	good
11.0	$(iso\text{-}C_4H_9)_2Al$ $(iso\text{-}C_4H_9O)$	—	—	11.0	very poor
11.0	»	2.0	$(iso\text{-}C_4H_9)AlCl_2$	11.0	good

* Carefully freed from hydride.

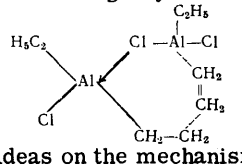
regarding the reducing role of AlR_3 in the formation of an active catalyst complex for ethylene polymerisation.

From this viewpoint, work on the catalytic activity of organometallic complexes in the polymerisation of ethylene[26-27] deserves special attention. It was shown that the interaction of $TiCl_4$ and $2(C_2H_5)_2AlCl$ in benzene solution at 25° in an atmosphere of nitrogen leads to the formation of a brown precipitate, consisting mainly of $TiCl_3$, and gaseous products containing ethane and only small amounts of H_2, C_4H_{10} and C_4H_8. With high values of the $R_3Al : TiCl_4$ ratio, the formation of a small amount of C_2H_4 was also noted. The filtrate consisted of unconverted $(C_2H_5)_2AlCl$ and a certain amount of an organoaluminium compounds of higher molecular weight. The presence of the latter compounds was demonstrated experimentally by oxidation and subsequent hydrolysis to form the corresponding primary aliphatic alcohols with molecular weights of about 400. The catalyst system $(C_2H_5)AlCl_2 + TiCl_4$ was also investigated. Mainly $TiCl_3$ and ethane were formed in the reaction of the components under the above conditions. The polymerisation of ethylene with this catalyst system at -10° gave only a low molecular product (average molecular weight 400).

Helden *et al.*[26-27] consider that ethane appears in the complex-formation reaction as a result of intramolecular disproportionation and hydrogen abstraction. The overall reaction may be represented in the following way:



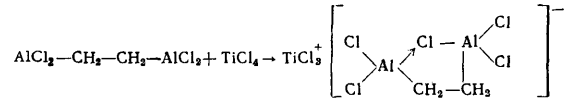
The authors believe that the aluminium compound initiates the polymerisation reaction. The role of $TiCl_3$ formed by the reduction of $TiCl_4$ is not presented clearly enough. It is only shown to "stabilise" the formation of the organoaluminium compound, the structure of which was given above. Chain growth was assumed to take place through the Al–C bond in the following way:



Using the above ideas on the mechanism of the formation and action of organometallic polymerisation catalysts, the same authors proposed a new catalyst system ($AlCl_3$, K, and $TiCl_4$) for ethylene. $AlCl_3$ and K, suspended in heptane (1–2 : 1), react in the presence of ethylene to form a dark-grey solid product. The addition of $TiCl_4$ leads to the rapid polymerisation of ethylene (reaction temperature 65°, atmospheric pressure). It is assumed that in the interaction of $AlCl_3$ and K, the $AlCl_3$ is partly reduced. The subhalide derivatives of aluminium formed (their formation was confirmed by decomposition of the product with water) react with ethylene giving a compound of the type $AlCl_2$-$-C_2H_4$-$AlCl_2$. The structure of this compound was confirmed by the formation of dideuteroethane ($C_2H_4D_2$) on decomposition with deuterated water and also by analogy with the previously known compound with the structure BCl_2-$-C_2H_4$-BCl_2. The compound $AlCl_2$-C_2H_4-$AlCl_2$ was extracted with ether which resulted in the formation of Al_2Cl_4.C_2H_4.$2(C_2H_5)_2O$. The diether derivative obtained was active in the polymerisation of ethylene only in conjunction with $AlCl_3$ (2 moles per mole of diether derivative). The authors consider that this is explained by the following reactions.

$$2AlCl_3 + AlCl_2\text{-}C_2H_4\text{-}AlCl_2.2(C_2H_5)_2O \rightarrow$$
$$\rightarrow 2AlCl_3.(C_2H_5)_2O + AlCl_2\text{-}C_2H_4\text{-}AlCl_2.$$

An active catalyst complex is formed by the interaction of this compound with $TiCl_4$.



Chain growth proceeds in the same way as described above.

In connection with the experimental data and theories of the Dutch investigators it should be noted that the activity of the catalyst $AlCl_3 + LiAlH_4 + TiCl_4$ in the polymerisation of ethylene had been established earlier by us[28]. In this case $LiAlH_4$ is an even better reducing agent than K which was used in the investigations described above. In contrast to the Dutch workers, the present authors believe that the intermediate formation of R_3Al, by the reaction of $AlCl_3$, $LiAlH_4$, and C_2H_4 is more likely. We did not study the reaction mechanism, but established experimentally the high activity of the proposed new catalyst system not only for the polymerisation of ethylene but also for the synthesis of stereoregular polypropylene.

The experimental investigation of the polymerisation of ethylene and propene in the presence of powdered aluminium and $TiCl_4$, described quite recently by Japanese authors[29,30], is extremely interesting. In the polymerisation of ethylene this catalyst leads to the formation of linear polymers with a melting point of 130° and a molecular weight $(30-40) \times 10^3$. It was also established that the addition of $TiCl_3$ to the Al–$TiCl_4$ system considerably affected the properties of the polymer obtained, especially its molecular weight, which in this instance increased to 300×10^3. It is interesting that according to the authors' data, turnings may be used successfully instead of powdered aluminium, which of course is of considerable interest from the point of view of possible practical application of the reaction to obtain polyethylene.

In a study of the activities of titanium chlorides, it was shown that the highest activity is displayed by $TiCl_4$ which the authors explain by its high Lewis acidity.

In the polymerisation of ethylene a solid polymer is obtained in good yield only when an alloy of Al and Mg is used. Variation in reaction conditions (temperature, pressure, and proportions of the catalyst components) can affect the properties of the polyethylene in the same way as the polymerisation of ethylene is controlled in the presence of a typical Ziegler catalyst. On the basis of experimental data, the following equation for the rate of polymerisation is proposed:

$$-\frac{dP}{dt} = 4.37\,[TiCl_4]\exp(-4800/RT)P.$$

From the equation it is clear that, other conditions being equal, the reaction rate is determined only by the concentration of $TiCl_4$ and does not depend on the amount of Al. On this basis the authors consider a cationic mechanism the most likely and do not give it further consideration. We suggest that in this instance one may expect the formation

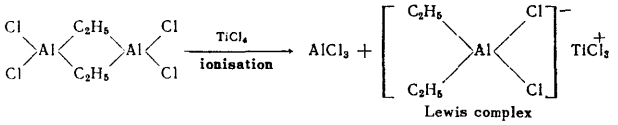
of an intermediate organoaluminium compound which subsequently yields the active catalyst complex.

In order to obtain reproducible results in polymerisation with the $R_3Al + TiCl_4$ catalyst system, a high degree of purity of the monomer and the solvent in which the polymerisation is carried out is essential[11]. It is also shown that to ensure the formation of an active complex it is necessary to introduce the components of the catalyst system in a sequence which will result in the minimum formation of R_2AlCl as this is less active than R_3Al. However, according to a number of other publications, R_2AlCl has an activity equal to, or even higher than, that of R_3Al in the polymerisation of ethylene and propene.

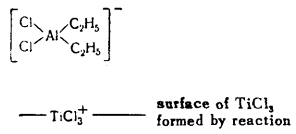
One investigator[31] has proposed the following mechanism for the interaction $(C_2H_5)_2AlCl$, and $TiCl_4$:

$$(C_2H_5)_2AlCl + 2TiCl_4 \rightarrow (C_2H_5)AlCl_2 + TiCl_3' + TiCl_4 + C_2H_5. \quad (1)$$

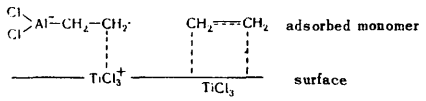
$(C_2H_5)AlCl_2$ exists in dimeric form:



The complex formed is adsorbed on the solid surface of $TiCl_3$ through $TiCl_3^+$ ions:



Later, evidently through intermolecular disproportionation, ethane is evolved and an active centre for the growth of a polymer chain is established:



The monomer is adsorbed on the surface of $TiCl_3$ and is polymerised by means of the ion-radical of the active complex. Although this mechanism is not substantiated by experiment, we believe it to be more probable than the similar idea put forward by Helden and coworkers[26,27] and discussed above.

Several investigators consider that the catalytic activity of R_3Al is directly connected with its reducing power with respect to $TiCl_4$.[32] The authors show that the substitution of one ethyl group by an ethoxy-group leads to the formation of a compound which does not reduce $TiCl_4$ at all. However, no experimental data have been reported, which would suggest that the organometallic compound obtained has no catalytic activity.

It is interesting to note that an excess of $TiCl_4$ in the catalyst system leads to a substantial reduction in the molecular weight of the polyethylene. A similar effect takes place when $(C_2H_5)_2AlCl$ is introduced into the catalyst composition, which agrees well with earlier data[8]. The observed lowering of molecular weight of the polymer is explained in different ways. Some consider[8] that with excess $TiCl_4$ the following reaction occurs:

$$R_3Al + 2TiCl_4 \rightarrow RAlCl_2 + 2RTiCl_3.$$

The compound $RAlCl_2$ causes less decomposition of $RTiCl_3$ with the formation of $TiCl_3$ than does R_2AlCl; since according to these authors the organotitanium compound leads to the formation of a low-molecular polymer, this explains the effect observed with excess $TiCl_4$.

On the other hand[32], it is suggested that the lowering of the molecular weight of the polymer in the presence of excess $TiCl_4$ is due to the breaking of a growing polymer chain by a chloride ion:

$$TiCl_4 \rightleftharpoons TiCl_3^+ + Cl^-,$$

$$M^+ - CH_2 - CH_2 - CH_2 - CH_2 - \sim\sim\sim + TiCl_3^+ + Cl^- \rightarrow$$
$$\rightarrow MCl + TiCl_3 - CH_2 - CH_2 - CH_2 - CH_2 - \sim\sim\sim.$$

Both explanations are hypothetical as they are not supported enough by experimental data. It may equally well be suggested that the excess $TiCl_4$ (and also the excess R_2AlCl) lead to the destruction of the high-molecular compound formed.

Comparison of the reduction of Ti^{4+} to Ti^{3+} by the action of R_3Al, R_2AlCl, and $RAlCl_2$ on $TiCl_4$ showed that the organoaluminium compound is not fully used up, even with a considerable excess of $TiCl_4$, evidently due to complex formation[33]. The reducing power of organoaluminium compounds increases in the series $(C_2H_5)AlCl_2 < (C_2H_5)_2AlCl < (C_2H_5)_3Al$, the change from $(C_2H_5)AlCl_2$ to $(C_2H_5)_2AlCl$ being insignificant, and very marked from $(C_2H_5)_2AlCl$ to $(C_2H_5)_3Al$. It is interesting that under the experimental conditions (80°) the reducing power calculated for one ethyl group remains practically the same for the series of organoaluminimum compounds investigated.

Similar observations were reported by other authors who also studied the interaction of various organoaluminium compounds with titanium halides[34,35]. It was found that in the interaction of $TiCl_4$ with R_3Al there is evidently formed a brown modification of $TiCl_3$ which is very reactive with respect to R_3Al. Unfortunately the conclusions of these authors, like many others, are not reliable enough owing to the fact that the R_3Al used contained other compounds which were not inert to $TiCl_4$. Thus the $(C_2H_5)_3Al$ used by Boldyreva *et al.*[35] contained according to analysis 80% $[(C_2H_5)_3Al + (C_2H_5)_2HAl]$ and 20% $(C_2H_5)_2AlOC_2H_5$. The purest organoaluminium compound was used by Roha and coworkers[18].

In all the papers quoted the interaction between $TiCl_4$ and the organoaluminium compounds is considered as an oxidation–reduction reaction. This is true only when there is a hydride ion in the organoaluminium compound; reduction of titanium and oxidation of the hydride ion then takes place:

$$2R_2HAl + 2TiCl_4 \rightarrow 2TiCl_3 + 2R_2AlCl + H_2.$$

In the other cases titanium tetrachloride is alkylated in the usual way with the formation of organotitanium compounds:

$$R_3AL + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl,$$
$$R_2AlCl + TiCl_4 \rightarrow RTiCl_3 + RAlCl_2,$$
$$RAlCl_2 + TiCl_4 \rightarrow RTiCl_3 + AlCl_3.$$

A paper was recently published which was devoted to the study of a new catalyst system, $R_3Al + CrCl_3$, in the stereospecific polymerisation of propene[36]. Chromium trichloride has a substantial advantage over titanium trichloride as it is inert to air. The experimental data show that the catalyst complex obtained with $CrCl_3$ has a lower activity, but is quite stereospecific. In this system $(C_2H_5)_3Al$ proved to be a more active component of the polymerisation catalyst than $(iso\text{-}C_4H_9)_3Al$ which was studied at

the same time. In view of the high activity of $TiCl_2$ in the polymerisation of ethylene reported above, it is interesting that $CrCl_2$ is practically inactive in the polymerisation of propene, as can be seen from the following data:

$CrCl_2 : CrCl_3$ Ratio	0.00	1.0	∞
% conversion of C_3H_6	16.0	9.0	0.0

The product of the interaction of $(C_2H_5)_2Zn$ and $TiCl_4$ was shown to be an active catalyst for the polymerisation of propene to a high molecular solid polymer[37]:

$$TiCl_4 + (C_2H_5)_2Zn \rightarrow TiCl_3 + C_2H_5ZnCl + C_2H_5^{\bullet}.$$

The highest percentage conversion of propene to polymeric oil was attained with equimolar proportions of $(C_2H_5)_2Zn$ and $TiCl_4$. With a threefold molar excess of $(C_2H_5)_2Zn$, solid polypropylene, which had a melting point 150°–158° and a molecular weight $(1.0–1.8) \times 10^4$, was formed in 30% yield; with a higher excess of $(C_2H_5)_2Zn$, the yield of solid polymer was appreciably lower. The authors[37] also established that the character of the radical in the organozinc compound had practically no effect on the activity of the catalyst system formed.

Interesting data were obtained in an investigation of the effect of nucleophilic organic compounds which could interact with both components of Ziegler catalysts[38]. The influence was studied of electron-donor additives (triethylamine, diphenylamine, aniline, and dimethylaniline) in the polymerisation of propene with the $(C_2H_5)_3Al + TiCl_3$ (molar ratio 3 : 1) catalyst system. It was found that the presence of a certain amount of amine led to a considerable increase in the molecular weight of the polypropylene.

The activating influence of amines, leading to a change in the relative rates of the growth and chain breaking processes, was also established. In some experiments, especially when halogen-substituted amines were used, an increase in the overall rate of polymerisation was observed. It is supposed that the electron pair of the amine can interact with the *d* shell of $TiCl_3$ to form bonds; this should be reflected in the electronic state of the adsorbed organometallic molecule and consequently in the energy of the active bond. The value of the latter determines the rate of the chain-propagation reactions and the probability of chain termination at the active bond to a considerable extent. For a fuller explanation of the role of amines, their interaction with R_3Al would also have to be studied, but this was not done.

Addition of small amounts of diphenylamine to the organometallic catalyst $(C_2H_5)_3Al + TiCl_4$ or $(C_2H_5)_2AlCl + TiCl_3$ in the polymerisation of 1-pentene increased the yield of polymer. However, increase in the diphenylamine above a certain amount inhibited the reaction. A similar effect was caused by tolylthiol[39].

It is well known that alkylaluminium forms complexes or co-ordination compounds with amines[40], for example, $Me_3Al^-.N^+Me_3$. It has been found that R_3Al readily forms co-ordination compounds with electron donors; therefore it is quite likely that the initial step in the interaction of R_3Al with $TiCl_4$ is the formation of complexes of the type $Cl_3Ti^+.R_3Al^-Cl$ or $Cl_2Ti^+.(R_3Al^-Cl)_2$.[41] These complexes are then decomposed with rupture of the Ti–Cl and Al–R bonds.

The experimental data of Cooper and Rose[41] are of interest in connection with the elucidation of the nature of the activity of organometallic catalyst complexes. They have shown that the activity of solid products, formed by the reaction of R_3Al and $TiCl_4$, is not reduced on drying in a vacuum. These solid products have a laminated structure, in which the chlorine layer is slightly modified through partial substitution of chloride ions by species such as $(C_2H_5)_3\overline{Al}Cl$, $(C_2H_5)_2\overline{Al}Cl_2$, or $(C_2H_5)\overline{Al}Cl_3$. These ions are formed by co-ordination of $(C_2H_5)_3Al$, $(C_2H_5)_2AlCl$, or $(C_2H_5)AlCl_2$ with chloride ions already present in the lattice. It is supposed that ethylene molecules combine with titanium atoms and then react with complex anions in the lattice:

$$Ti^{2+} \rightarrow \underset{\underset{CH_2}{\|}}{CH_2} + R_3Al^-Cl \rightarrow Ti^+CH_2CH_2R + R_2AlCl.$$

Chain growth then proceeds through introduction of olefine molecules at the Ti–C bond. The mechanism of chain transfer is similar to Ziegler's hypothesis[42] for the interaction of R_3Al with C_2H_4. This mechanism leads to R and $C=CH_2$ terminal groups in the polymer, which was confirmed experimentally by Natta and his coworkers[80]:

$$Ti^+CH_2CH_2R + nC_2H_4 \rightarrow Ti^+CH_2CH_2(CH_2CH_2)_nR,$$
$$Ti^+CH_2CH_2(CH_2CH_2)_nR + C_2H_4 \rightarrow Ti^+CH_2CH_3 + CH_2=CH(CH_2CH_2)_nR.$$

Other mechanism may also be proposed which entails the formation of similar terminal groups. In this case preliminary reduction of ethylene by divalent titanium is supposed, with the formation of a hydride ion which ultimately enters into the lattice:

$$Ti^{2+} + CH_2=CH_2 \rightarrow Ti^{3+}CH=CH_2 + H^-,$$
$$Ti^{3+}CH=CH_2 + nC_2H_4 \rightarrow Ti^{3+}(CH_2CH_2)_nCH=CH_2,$$
$$R_3Al^-Cl, + Ti^{3+}(CH_2CH_2)_nCH=CH_2 \rightarrow Ti^{2+} + {}_1R(CH_2CH_2)_nCH=CH_2 + R_2AlCl.$$

Both mechanisms require further experimental study.

Investigation of ethylene polymerisation in the presence of a catalyst complex, formed from $TiCl_4$ and $(C_4H_9)Li$ or $(C_4H_9)_2Zn$,[43] showed that the polymerisation rate was proportional to the amount of $TiCl_4$ and did not depend on the nature or the amount of metal alkyl. With a considerable excess of $(C_4H_9)_2Zn$, the reaction was inhibited. The reaction mechanism proposed, including the preliminary formation of a trivalent titanium alkyl-compound, followed by rupture of the Ti–C bond, was not verified by experiment.

Natta[2] considers that organometallic complex catalysts represent a special type of catalyst as in many cases they allow polymers to be obtained, having structures different from those previously known, even with atactic poly-α-olefines. In fact, investigation of the infra-red spectra showed that the new polymers of α-olefines have more regular structures (especially "head to tail" addition compounds) than the polymers obtained by other methods. Natta attributes this difference to the special co-ordination bonds in the catalyst. He considers that there can be no doubt that the activity of the better stereospecific catalysts in the polymerisation of α-olefines, is connected with the co-ordination activity of atoms of a strongly electropositive transition metal, distributed on the surface of the solid microcrystalline phase, which can chemisorb organometallic compounds.

The electropositivity of the transition metal atom increases as its valency decreases; therefore only low-valency compounds of the transition metals can take part in anionic co-ordination catalysis. Weakly electropositive

metals (for example, Pt, Pd, etc.) are inactive even in a low-valency state.

The following arguments are cited in support of the hypothesis of anionic co-ordination catalysis:

1. The regular linear macromolecules of "head to tail" structure, which are formed in the polymerisation of monomers of the type $CH_2=CHR$ may be explained by the greater tendency of the CH_2 group, compared with the CHR group, to give a carbanion which can enter into a co-ordination bond with an organometallic complex.
2. The poly-α-olefine macromolecules have vinylidene groups at one end of the chain, and alkyl groups, with the same number of carbon atoms as the normal chain of the olefine monomers, at the other[44].
3. In the most active catalysts there are at least two different metals, strongly electropositive and with the power to form complexes.
4. The greater catalytic activity of complexes containing metal ions with small radius and high local electric field (ionic radii: Be 0.35 Å, Al 0.51 Å, Li 0.68 Å).
5. The electrical conductivity of the ionic type, with migration of the more alkylated groups to the anode, which is shown by solutions of organometallic compounds (such as R_3Al) and by their catalytically active soluble complexes.
6. The reactivity of the monomers follows a sequence which is the reverse of that in cationic polymerisation. The reactivity of propene and butene is less than that of ethylene because of the presence of the CH_3 group.
7. The nature of chain growth,

$$(\text{complex}) - CH_2 - CHR - P + CH_2=CHR \rightarrow$$
$$\rightarrow (\text{complex}) - CH_2 - CHR - CH_2 - CHR - P,$$

and the nature of chain termination, which leads to the formation of a vinylidene bond through transfer of the hydride ion from the CHR group of the last monomer unit to the catalyst complex, which can then initiate a new polymer chain:

$$(\text{complex}) - CH_2 - CHR - P \rightarrow$$
$$\rightarrow (\text{complex}) - H + CH_2=CR - P,$$

$$(\text{complex}) - H + CH_2=CHR \rightarrow$$
$$\rightarrow (\text{complex}) - CH_2 - CH_2R.$$

This transfer takes place more easily, the better an electron donor group R is. In this way it is possible to explain the lower molecular weight of poly-α-olefines compared with polyethylene or polystyrene.

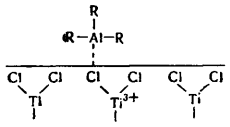
8. The fact that, in contrast to radical polymerisation, the molecular weight does not drop when the polymerisation is conducted in the presence of solvents which are capable of absorbing free radicals (for example, cumene, iso-octane, etc.).
9. The rate of polymerisation is constant when stable catalysts are used. In contrast to radical initiators, a solid catalyst is not used up.
10. The molecular weight is reduced with increase in the concentration of R_3Al.

Our experimental results[13,45] and the published data suggest that radical processes also play a definite part in the stereospecific polymerisation of α-olefines in the presence of complex catalysts. In general, we believe that it is impossible to determine definitely the mechanism by which the very complex reaction of polymerisation takes place in the presence of organometallic catalysts.

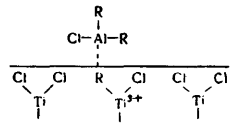
In the interaction of the components of a Ziegler type catalyst, alkylation of $TiCl_4$ first takes place, and then homolytic scission of the organotitanium compound formed:

$$TiCl_4 + R_3Al \rightarrow RTiCl_3 + R_2AlCl,$$
$$RTiCl_3 \rightarrow TiCl_3 + R^{\cdot}.$$

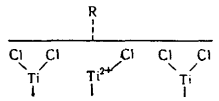
The radicals evolved recombine or disproportionate. The excess R_3Al in the system is adsorbed on the $TiCl_3$ crystal surface:



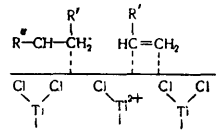
Then an exchange reaction takes place between $TiCl_3$ and aluminiumalkyl:



The organotitanium compound formed is decomposed with the formation of a radical, which is adsorbed on the surface:

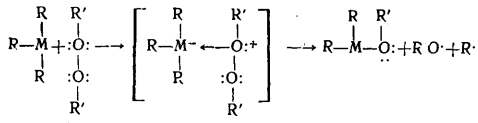


The radicals adsorbed on the surface will have different properties from ordinary free radicals. They may in fact initiate the polymerisation of monomer, which is adsorbed on the surface as well:



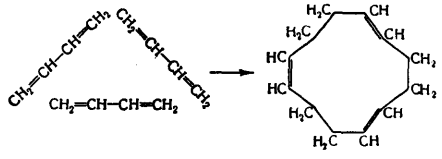
A recently published work by Japanese authors[46], concerning the additional catalytic effect of oxygen compounds on the polymerisation of vinyl monomers initiated by organometallic compounds is of interest. In this work the effect of molecular oxygen, peroxides (organic and inorganic), salts of silver, copper, and other auxiliary catalysts on the catalytic activity of organometallic compounds of boron, cadmium, zinc and aluminium was studied. It was shown that the behaviour of the oxygen compounds was connected with the nature of the central atom in the organometallic compound. A large accelerating effect was observed in polymerisation initiated by triethylboron. It should be noted that molecular oxygen, in an appropriate amount, accelerated polymerisation, but became an inhibitor when present in excess. These results suggest that molecular oxygen can react with organometallic compounds, forming an active radical, which initiates polymerisation. Excess O_2 breaks the radical chain in the same way as in ordinary radical polymerisation. The authors propose the following mechanism. They regard this type of polymerisation as a new form "redox" polymerisation. The

organometallic compound may react, for example with a peroxide, as follows:



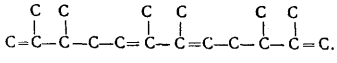
where M may be Al or B. The free radicals formed initiate polymerisation.

The experimental data of Wilke[47] indicating the exceptional selectivity of organometallic catalysts of the Ziegler type are of great theoretical and practical interest. The author showed that a catalyst, consisting of $TiCl_4$ and R_2AlCl, which polymerises ethylene to high-molecular polyethylene, converts butadiene almost exclusively to one specific oligomer. The elucidation of the structure of this oligomer, however, led to a far more important result. The authors had discovered that the ethylene polymerisation catalyst causes cyclisation of three molecules of butadiene into a ring and that the oligomer represents 1, 5, 9--cyclododecatriene.

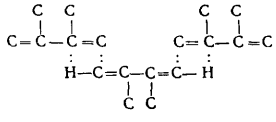


The oligomerisation process, with the catalysts indicated, takes place selectively to form a specific isomer. Thus, $TiCl_4 + R_2AlCl$ gives only *trans, trans, cis*-1, 5, 9--cyclododecatriene. Another cyclododecatriene isomer, for example, *trans, trans, trans*-1, 5, 9-cyclododecatriene, can be synthesised by using the $CrCl_3 + R_3Al$ catalyst system or R_2HAl. The study of the cyclisation of butadiene led the author to investigate the reaction of organometallic catalyst complexes with other conjugated diolefines such as isoprene, piperylene and 2, 3-dimethylbuta-1, 3-diene. In the course of this investigation a new kind of addition mechanism by conjugated diolefine monomers was discovered.

It was shown that 2, 3-dimethylbuta-1, 3-diene reacts with a chromium catalyst; the reaction product is not however, a homologue of cyclodecatriene, but an open--chain trimer of dimethylbutadiene. The structure of this compound was established by means of infra-red spectroscopy:



The oligomer was formed by addition of the H−C = groups of the middle molecule to the double bonds of the two end molecules:



This addition mechanism with hydrogen transfer in the interaction of organometallic catalyst complexes with conjugated diolefines had not been observed until recently. The situation becomes more complicated in the case of isoprene, which reacts partly like butadiene and partly like dimethylbutadiene.

The polymerisation of unsaturated hydrocarbons in the so-called canal compounds[48] offers considerable interest as regards the elucidation of the nature of sterospecific polymerisation and the conditions necessary to effect it. Therefore, although this goes somewhat beyond the scope of the present paper, we shall now turn our attention to the polymerisation of unsaturated hydrocarbons in the presence of such systems. It was found that 2, 3-dimethylbuta-1, 3-diene forms a molecular canal compound with thiourea in which the monomer is polymerised. The rate of formation of the canal compound and the rate of polymerisation depend on the purity of the reagents used.

The canal polymer obtained is in the form of white flakes which on drying in air become grey and melt at 175°−225°. After prolonged water treatment the polymer contained approximately 2.5% S and 2.2% N. It thus appears that every hundredth thiourea molecule participates in the polymerisation. Five high-molecular crystalline polymers, synthesised by irradiating the monomer oriented in urea canal complexes have also been described[49]. These were polybutadiene, polyacrylonitrile, polyacrolein, polyvinyl chloride and a copolymer of vinylchloride and acrylonitrile. Canal polymerisation was studied in the case of 13 different compounds altogether. The authors believe that isotactic and syndiotatic polymers can be obtained in this way. From our point of view the possibility of polymerisation with optically active urea deserves special attention. White and Brown[49] suggested that optically active polymers might be synthesised in this way from inactive monomers. Unfortunately in the last 3−4 years no new data have been obtained in the field of canal polymerisation, and the subject has received little attention.

In recent years, a number of papers, devoted to stereospecific polymerisation of unsaturated compounds containing polar groups have been published. It was shown that under certain conditions the stereospecific polymerisation of a variety of unsaturated compounds, not only of the hydrocarbon series, is practicable. Using the common catalyst system $R_3Al + TiCl_3$ in a saturated hydrocarbon medium, crystalline stereoregular polyvinyl chloride was obtained successfully[50]. It was shown that to form more stable catalyst complexes, it is expedient to use certain complex-forming additives, for example, ethyl ether, dioxane, amines.

4. SOLUBLE ORGANOMETALLIC COMPLEX POLYMERISATION CATALYSTS

The typical Ziegler catalysts considered above are insoluble in the reaction medium. In recent years interest has arisen in the study of completely soluble polymerisation catalysts.

This is because comparison of the catalytic activity of homogeneous and heterogeneous catalysts gives a definite answer to the very important question whether the success of polymerisation depends on the presence of a solid surface. Up to the present, many investigators have held the opinion that Ziegler catalysts owe their high activity to their heterogeneity. Moreover, the presence of a solid surface presents the greatest difficulty in studying the process mechanism. The study of the kinetics in a homogeneous medium makes it possible to avoid this.

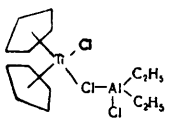
Polymerisation by soluble catalysts has also certain practical advantages. Each ionic bond in the soluble complex can react with the monomer and initiate the growth of

a polymer chain. With a heterogeneous catalyst, only a small part, directly on the surface, is active. By virtue of this the consumption of a homogeneous catalyst is far less. In addition, unreacted catalyst is not left contaminating the polymer and this considerably eases the cleaning of the polymer – a very laborious step in the manufacturing process. In this case also, there is no danger of deactivating the catalyst through it being blocked by the polymer. Soluble catalysts give a far narrower molecular weight distribution in the polymer since in the course of polymerisation the amount of catalyst remains relatively constant.

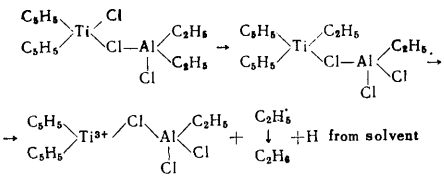
Natta[51] and Breslow[52] first reported the soluble complex compounds which are formed from $(C_5H_5)_2TiCl_2$ and organic aluminium compounds and are active in the polymerisation of ethylene to high-molecular products. It was shown[53] that in a solution of the complex, titanium is present in the trivalent state. Reduction of Ti^{4+} evidently involves three steps: (1) formation of a complex between the "sandwich" dichloride and the aluminiumalkyl compounds; (2) alkylation of the "sandwich" dichloride; (3) homolytic scission of the alkyl–titanium bond. The first stage of complex formation takes place very rapidly:

$$2(C_5H_5)_2TiCl_2 + 2(C_2H_5)_2AlCl \rightleftharpoons 2(C_5H_5)_2TiCl_2.(C_2H_5)_2AlCl.$$

One possible structure of the complex is



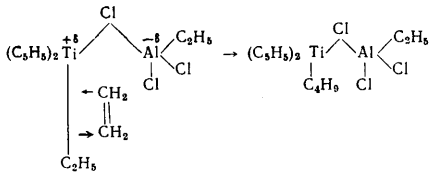
The complex is far more soluble in hydrocarbons than the original "sandwich" compound. This indicates that the bond in the complex is covalent:



The second and third stages are rather complicated. For instance, it is not clear why $(C_2H_5)_3Al$ causes very rapid reduction but $(C_2H_5)_2AlCl$ is slow-acting. Evidently, the stability of the Ti–C bond depends on the type of compound with which complex formation takes place, or it is possible that reduction involves dialkylation, and $(C_2H_5)_3Al$ is a more powerful alkylating agent than $(C_2H_5)_2AlCl$.

The complex of trivalent titanium is a very poor ethylene polymerisation catalyst. This is in keeping with the data of Natta[50] regarding the complex obtained with $(C_2H_5)_3Al$. However, a fresh mixture of $(C_5H_5)_2TiCl_2$ and $(C_2H_5)_2AlCl$ becomes a very active catalyst if the ethylene contains traces of oxygen. In the latter case a change in the colour shows quite definitely that the oxygen leads to the formation of a compound of tetravalent titanium. In this way it was established that in order for the given soluble catalytic system to be highly active, it must contain a certain amount of tetravalent titanium. However, it has not yet been demonstrated whether the presence of Ti^{4+} is the only requirement or whether a mixture of Ti^{4+} and Ti^{3+} is needed for high activity.

The active form of the catalyst is possibly the compound $(C_5H_5)_2Ti^{4+}(C_2H_5)Cl.(C_2H_5)AlCl_2$ or the product of its interaction with ethylene[53,54]. Growth of the polymer chain takes place by the introduction of a monomer molecule between the alkyl group and Ti:



The first stage of the polymerisation evidently includes the formation of a π-complex between titanium and the olefine. All co-ordination potentialities of aluminium are already exhausted and therefore formation of a complex of olefine and aluminium is improbable. The function of R_3Al is to alkylate Ti and by subsequent redistribution of electrons to increase the power of titanium to form complexes.

The second step is the conversion of an ethyl group (or a long alkyl chain in a growing polymer) to ethylene and the formation of a new titanium–carbon bond. Chain growth on a titanium atom seems all the more likely as catalytic polymerisation systems which include only titanium compounds are known. Thus, the products of irradiated $TiCl_4$ can by themselves polymerise ethylene to a high-molecular product[55]. R_3Al may be replaced successfully by other reducing agents, including the alkyls of alkali metals[56–59]. However, additional evidence is required on this point.

With compounds of titanium (or other transition metals) of the lowest valency, a more stable metal–carbon bond is realised. This in turn increases the life of the active centres and consequently leads to polymers of higher molecular weight being obtained.

On the other hand, from what has been said above, the formation of a highly active catalyst requires that a certain amount of Ti^{4+} be present. This was confirmed by a study of the kinetics of ethylene polymerisation by the $(C_5H_5)_2.TiCl_2 + (CH_3)_2AlCl$.[60] The process of chain initiation includes the rapid reaction of the catalyst components to form an inactive complex, which is then transformed into a complex possessing catalytic activity. This process takes place with measurable speed. The rate constant of initiation depends on the Al : Ti ratio, and as this increases, initiation takes place more slowly.

Three types of structure may be postulated for the active complex, differing mainly in the position of the alkyl groups which are involved in the growth of the polymer chain: (1) the alkyl groups bridge the Ti and Al atoms; (2) the alkyl groups are joined only to Ti; (3) the alkyl groups are joined only to Al.

The first two possibilities are the most likely, since, as was already noted in section 2, catalytic systems are known which consist only of titanium compounds, for example: CH_3TiCl_3, $CH_3TiCl_3–TiCl_3$, $(C_5H_5)_2Ti(C_6H_5)_2–TiCl_4$, etc. The function of R_3Al consists of alkylating Ti^{4+}. In addition, R_3Al acts as a Lewis acid, producing a deficit of electrons in the titanium and thus facilitating the complex formation between titanium and ethylene.

The chain-propagation stage includes the formation of a complex by the overlapping of the ethylene π electrons with the 3*d* orbitals in titanium. This is followed by displacement of an alkyl group from Ti to C_2H_4 and conversion of the link between the latter and Ti to a σ bond. All this agrees with the mechanism discussed before[53]. The total

activation energy of the polymerisation of ethylene with the catalytic system $(C_5H_5)_2TiCl_2$ + $(CH_3)_2AlCl$ was found to be 11.75 kcal mole^{-1}.

It was shown that on average each methyl group taking part in the initiation of a polymer chain gives one polymer molecule. The number of polymer molecules formed on $(C_5H_5)_2TiCl_2$ is usually greater than unity, and it increases with increasing Al : Ti ratio. Thus it is evident that Ti^{4+}, before it is reduced to Ti^{3+} with homolytic scission of the Ti–C bond, takes part in the initiation and growth of more than one macromolecule. The trivalent titanium complex is not a catalyst for the polymerisation of ethylene at room temperature and atmospheric pressure.

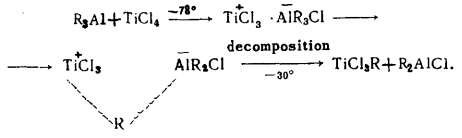
In work with a complex labelled with a ^{14}C atom it was established that rupture of the Ti–C bond is followed by disproprortionation, and not recombination, of the alkyl radicals formed.

Table 3 shows the principal properties of polyethylene, obtained with the soluble catalyst system $(C_5H_5)_2TiCl_2$ + + $(C_2H_5)_2AlCl$. The properties of polyethylene, obtained with a heterogeneous Ziegler catalyst, are given for comparison. It is evident that the soluble catalyst forms a highly linear polymer with a higher melting point and a considerably narrower molecular weight distribution.

In the light of the work on soluble complexes discussed above, it may be concluded that the presence of a solid surface is not a requisite condition for the catalytic polymerisation of ethylene to a high-molecular product.

In an investigation of the soluble catalyst system $(C_5H_5)_2$. $TiCl_3$ + R_3Al in ethylene polymerisation[61], it was found that the catalyst was only active when a certain amount of HCl was added. Evidently, this is related to the data discussed above, regarding the role of electrophilic reagents in the formation of an active organometallic catalyst. The polyethylene obtained with this catalyst system has practically the same properties as the polymer synthesised with ordinary Ziegler catalysts.

Soluble complexes of $TiCl_4$ and R_3Al formed at low temperatures are also known[62]. It is thought that this occurs by the addition of a chlorine atom to aluminiumalkyl.



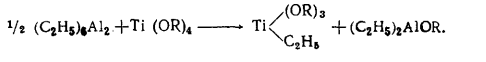
On decomposition of the complex the stable Al–C bond is broken and the less stable Ti–C bond is formed.

TABLE 3.

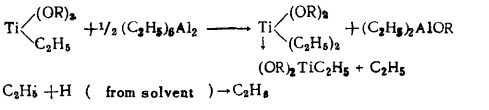
Properties of polyethylene	Soluble catalyst	Ziegler catalyst
Intrinsic viscosity	2.3	2.3
Melting point, °C	137	132
Crystallinity, %	85	79
$\bar{M}_w/\bar{M}_n$	3.6	7.0
Methyl groups, %	0.05	0.86
Vinyl groups, %	0.036	0.044
Vinylidene groups, %	0.006	0.007

Under these conditions, with the soluble $(iso\text{-}C_4H_9)_3Al$ + + $TiCl_4$ catalyst complex, a fairly constant rate of polymerisation of ethylene was observed. Curiously, determination of the valency state of titanium in the soluble complex at -78° showed that about 90% Ti^{4+} was present. Partial reduction might have occurred through small amounts of hydride present in the aluminiumalkyl. It was shown experimentally that it was not necessary for the entire polymerisation process to be carried out at the low temperature, which is needed to ensure sufficient stability of the soluble complex being formed. A low temperature is required only at the beginning of the polymerisation reaction; when chain growth has started on all the catalytic centres (this is observed visually by the disappearance of the dark-red colour from the reaction medium), polymerisation can be continued successfully at room temperature. The polyethylene obtained in this way has a melting point of 128°–130° and 80% crystallinity. At -75° propene was either not polymerised at all or showed only traces of polymer, but at a higher temperature, -20° to -30°, a polymer was formed. The properties of the product were not determined[62]. Nevertheless the polymerisation of propene in the presence of soluble catalyst complexes is of very great interest in extending our ideas on the nature of stereospecific catalysis and the role of surface effects in it.

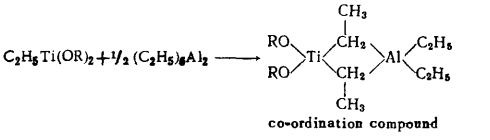
In the study of the kinetics of ethylene polymerisation in the presence of R_3Al and s-butyl titanate[63], it was found that the most active catalyst is formed with an $(C_2H_5)_3Al$: : titanium ratio of 3 : 1. The authors explain this by the fact that interaction between the catalyst components takes place in the following way:



Formation of the insoluble titanite $Ti(OR)_3$ was not observed, the catalytic system remaining homogeneous throughout.



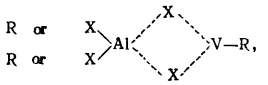
Later alkyl titanite is co-ordinated to a third molecule of aluminiumalkyl:



The co-ordination compound formed is an active catalyst complex with electron-deficient bonds, which is a general feature of catalyst systems of this type. Inhibition by alkyl halides, alcohols, and other polar molecules is explained by their interaction with the active complex and breakdown of the latter.

The authors[63] assert, albeit without any evidence, that homogeneous co-ordination compounds of this type can behave like the heterogeneous catalyst used in stereospecific polymerisation. However, Natta[64] found that the $Ti(OR)_4$ + + $(C_2H_5)_3Al$ catalyst complex, active in the polymerisation of ethylene, did not catalyse the polymerisation of propene. In our opinion this is due to the fact that reaction conditions (temperature, pressure, etc.) had not been found in which the polymerisation of propene becomes feasible.

According to Carrick's data[65,66], vanadium chloride may be employed instead of $TiCl_4$ in the formation of an active complex for the polymerisation of ethylene. A catalyst complex was formed by the interaction of $AlBr_3$, an organoaluminium compound [$(C_6H_5)_3Al$ or (iso-$C_4H_9)_3Al$], and vanadium chloride in a cyclohexane medium. The following structure is ascribed to the soluble catalyst complex:



where X—halide, R—aryl or alkyl radical.

Polarographic analysis established that the vanadium is present in the catalytic complex in the divalent state. It is stated that the function of the R_3Al in the formation of the catalyst complex is confined to reducing the vanadium to the divalent state and alkylating it in order to obtain the active form of the catalyst—RVX. These data are in good agreement with the above observations on the polymerisation of ethylene with R_3Al and the halides of titanium[14]. The role of $AlBr_3$ is to dissolve and stabilise the active vanadium part of the complex. In addition the $AlBr_3$ prevents further reduction of the vanadium. The polymerisation of ethylene with the vanadium catalyst complex was carried out at atmospheric pressure at 60°. The polyethylene obtained is highly linear (one methyl group per 1000 C atoms) and contains few double bonds (less than one C = C bond per 5000 C atoms). Propene and other α-olefines are not polymerised with this catalyst.

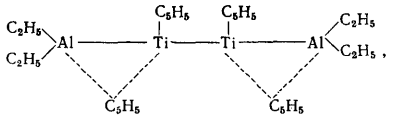
In order to explain the true nature of the active polymerisation centres in organometallic complex catalysts, Natta[67] and coworkers isolated three complexes in the pure state by crystallisation from solution. These contained titanium and aluminium with the general formula $(C_5H_5)_2.TiCl_2AlR_1R_2$, where R_1 and R_2 are chlorine atoms or ethyl groups. Some physical properties are given in Table 4. All the complexes are easily soluble in aromatic hydrocarbons and can be crystallised from n-heptane.

From a study of the chemical properties of these compounds and X-ray examination of their lattice structure, the authors concluded that two cyclopentadienyl nuclei are joined to a titanium atom whilst the latter is joined to aluminium through two chlorine bridges. The presence of chlorine bridges was also confirmed by reaction with trimethylamine.

All three complexes initiate the polymerisation of ethylene to form high-molecular polymers. However, the complex which does not contain alkyl groups shows extremely low activity. With the complexes containing ethyl groups, it was found by means of ^{14}C labelled alkyl groups, that each polymer chain contains one ethyl group originally present in the complex. Similarly with the complex containing four chlorine atoms in the molecule, $(C_5H_5)_2TiCl_2.AlCl_2$, it was established by means of labelled cyclopentadienyl groups that these groups were present in the polymer chains. Therefore, polymerisation of ethylene by the above complexes takes place *via* an anionic co-ordination mechanism through the introduction of monomer molecules at the organometallic bonds Al—C or Ti—C.

With increase in the number of alkyl groups in the complexes, their cationic activity is increased and they become capable of initiating the stereospecific polymerisation of vinyl ethers[68]. The complex $(C_5H_5)_2TiCl_2(C_2H_5)AlCl$ is an example of a catalyst capable of initiating stereospecific polymerisation by two different mechanisms, cationic and anionic, depending on the capacity of the monomers to be polymerised by one or other of the mechanisms.

By interaction of $(C_5H_5)_2TiCl$ in benzene at 80° with excess $(C_2H_5)_3Al$, a red crystalline product was obtained, which dissolved readily in aromatic hydrocarbons and melted (with decomposition) at 169°—171°. Chemical analysis and molecular-weight determination indicated that the compound had the formula $[(C_5H_5)_2Ti(C_2H_5)_2Al]_2$,[69] in which two cyclopentadienyl rings are joined to an atom of titanium. X-Ray examination showed that two types of cyclopentadienyl groups were present in this compound, two being joined to Ti atoms by means of σ, π-bonds and two joined to Al by σ, σ-bonds. The position of the latter two cyclopentadienyl groups suggests that they may be connected by a bridge both to Ti and to Al and in addition by π-bonds to Ti. The complex possesses diamagnetic properties owing to the presence of the Ti—Ti bond. Each Ti atom, moreover, gives up an electron pair to an Al atom, forming a dative Ti—Al bond.



The tricentric electron-deficient bonds are denoted by broken lines.

The complex is a catalyst for the polymerisation of ethylene to high-molecular products and in conjunction with α-$TiCl_3$ forms a catalyst system, which initiates highly stereospecific polymerisation of propene (the polypropylene contains far more isotactic molecules of high molecular weight than with the ordinary catalyst system $(C_2H_5)_3Al$ + + α-$TiCl_3$). The higher stereospecificity and the higher degree of polymerisation may be attributed to the fact that here chain transfer between the growing polymer chain and alkyl groups present in the catalyst system is more restricted.

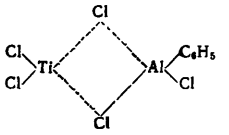
The complex with the general formula $Al_2TiCl_8C_6H_5$ [70] was also obtained by reaction of $TiCl_4$, $AlCl_3$, Al and benzene on heating to 80° for 7 h. This complex melts at 110°—115° (with decomposition), is easily dissolved in benzene and toluene, and is slightly soluble in aliphatic hydrocarbons. In the presence of oxygen and moist air it gives off HCl and phenol and with water in the absence of oxygen it yields benzene. This indicates that the phenyl group is joined to metal by a σ-bond. By decomposing the complex with dilute HCl and titrating with iron sulphate it

TABLE 4.

Complex	M.p., °C	Magnetic moment*
$(C_5H_5)_2TiCl_2Al(C_2H_5)_2$	126—130	1.70
$(C_5H_5)_2TiCl_2AlC_2H_5Cl$	88—92	1.57
$(C_5H_5)_2TiCl_2AlCl_2$	155—160	1.72

* Trivalent titanium has one unpaired electron in the *d* orbital and this is the cause of the paramagnetic properties of the complexes.

was established that the titanium is in the trivalent state. On treating the complex with compounds containing a free electron pair, such as tetrahydrofuran, dibutyl ether, pyridine, or trimethylamine at room temperature, the loss of one molecule of $AlCl_3$ was observed. This accords with the formula $[AlTiCl_5C_6H_5].AlCl_3$:

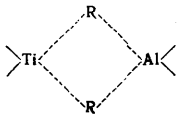


This complex, suspended in heptane, catalyses the polymerisation of ethylene, with the formation of a low-molecular fraction along with crystalline polymers of high molecular weight. The solid microcrystalline complex $AlTiCl_5C_6H_5$ polymerises ethylene at a higher rate than does $[AlTiCl_5C_6H_5].AlCl_3$. In this, only high-molecular polymers are obtained. The complex is also an active catalyst in the polymerisation of propene. The polypropylene formed contains isotactic, stereo-block, and atactic fractions. The following mechanism is proposed for polymer chain growth in the presence of the complex $AlTiCl_5.C_6H_5$:

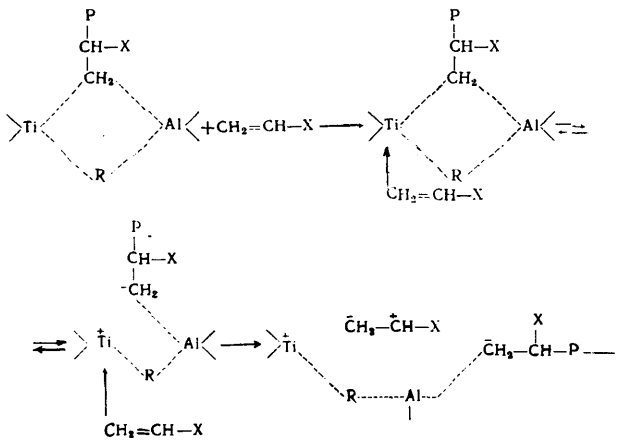
$$(TiAlCl_5)^+C_6H_5^- + CH_2=CH-CH_3 \rightarrow (TiAlCl_5)^+CH_2^- - \underset{CH_3}{\underset{|}{CH}} - C_6H_5.$$

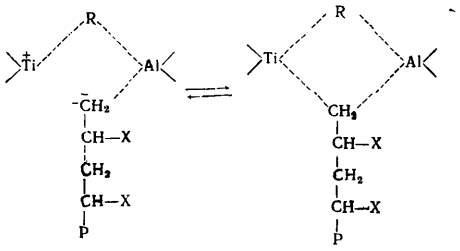
The presence of phenyl groups in the polymer chains was confirmed by infra-red spectroscopic analysis.

From the above discussion, a definite conclusion may be reached: all active polymerisation catalysts are electron-deficient organometallic complexes, which contain at least two metal atoms in their molecules, and polymerisation takes place by introduction of a monomer molecule in the bridge formed by alkyl groups between Ti and Al by means of tricentric bonds:



In this case it is difficult to determine whether the chain grows on the Ti or on the Al atom.





The first stage in monomer addition to the complex is determined by the high electron density in the double bond and a deficiency of electrons in the transition-metal complex.

However, until now the question of the valency of the transition metal in the active form of the catalyst complex remains unsolved. Some investigators[43] think that the catalyst owes its activity to trivalent titanium: others[14] quote experimental data showing that the most active valency state of titanium in the formation of a catalyst complex is Ti^{2+}; a third group[53] points to the necessity for heterovalent titanium (a mixture of Ti^{3+} and Ti^{4+}) to be present.

All the same, it is evident that it is not the valency state of titanium which is responsible for the catalytic activity but the presence of an electron-deficient bridge bond between Ti and Al. The valency state of the transition metal exerts a substantial effect on the stability of the metal–carbon bond. A reduction in valency leads to the formation of a more stable bond[17] and consequently to a longer life of the active centres.

It has been established that even stereospecific polymerisation, with the exception of polymerisation of α-olefines, does not necessarily require the presence of a solid phase. Thus isotactic and syndiotactic polymers were obtained from diolefines using soluble catalysts, formed by reaction between chromium acetylacetonate and R_3Al.[72]

Soluble catalysts are also known for the stereospecific polymerisation of alkyl vinyl ethers[68]. These compounds, such as $(R_2AlCl)_2$, $TiCl_2(OR)_2$, products of the reaction between $(C_5H_5)TiCl_2$ and R_3Al, etc. have weak cationic activity.

When the monomer contains two electron-rich groups (two double bonds in diolefines or one double bond and one oxygen with a pair of free electrons in vinyl ethers), then before addition of the monomer to the growing polymer chain, it associates with the electron-deficient catalyst, even if the catalyst does not contain a heterogeneous phase capable of adsorbing the monomer. This explains the stereospecific nature of the process in the presence of soluble catalyst complexes.

TABLE 5. Properties of methylmethacrylate polymers.

Type of solvent	Polymer properties		Density of Polymer at 30° (amorph) g ml^{-1}	Suggested chain configuration
	vitrification temp., °C	M.p., °C		
Strongly solvating	115	>200	1.19	isotactic
Weakly solvating	45	160	1.22	syndiotactic
Moderately solvating	60—95	170	1.20—1.22	stereo-block polymer

In the homogeneous catalytic polymerisation of methyl methacrylate with butyllithium or other organolithium compounds polymers of regular structure were also obtained (reaction temperature -50° to -80°).[73] It was shown that the nature of the reaction medium exerts a considerable influence on the stereospecific nature of the polymer. Thus, with a weakly solvating medium (toluene or hexane), isotactic polymethacrylate is formed but in a pyridine medium a syndiotactic polymer is obtained. In moderately solvating medium a stereo-block polymer is formed.

As was shown for the stereospecific polymerisation of methyl methacrylate, it is possible to use not only organolithium compounds, for example lithium fluorenyl, but also, apparently, other homogeneous catalyst systems[74]. Various types of stereoregular polymers were obtained in solvents of different solvating power.

5. THE ROLE OF PREVIOUS ORDERING OF THE MONOMER IN THE FORMATION OF THE POLYMER CHAIN MICROSTRUCTURE

Work carried out in recent years by Soviet investigators has demonstrated the role of previous ordering of the monomer in the formation of the polymer chain microstructure. The initiating power of certain metals in molecular mixtures with monomers[75] was investigated by applying for the first time the method of molecular beams in the polymerisation reaction. It was found that rapid low-temperature block polymerisation took place in molecular mixtures of metallic magnesium with a series of monomers (acrylonitrile, methyl methacrylate, methyl acrylate).

Polymerisation of acrylonitrile in the presence of magnesium in a frozen molecular mixture was studied by means of electron spin resonance[76]. It was shown that in this system polymerisation takes place by a radical mechanism. The formation of radicals, so the authors presume, occurs by interaction of the monomer vapour and magnesium:

$$CH_2=\underset{\underset{C\equiv N}{|}}{CN} + Mg \rightarrow Mg^+-\bar{C}H_2-\underset{\underset{C\equiv N}{|}}{CH}$$

These radicals together with excess of the monomer are condensed on a surface cooled by liquid nitrogen, and initiate polymerisation in the frozen mixture. However, we think that this hypothesis has not yet been supported by enough experimental data and the mechanism of this very interesting reaction should be investigated further. The fact that the polymethylmethacrylate obtained by this method has an isotactic structure deserves special attention. Until now only a syndiotactic polymer could be obtained from methacrylate by ordinary radical polymerisation.

Interesting data were also obtained in the study of the polymerisation of styrene with the $R_3Al + TiCl_3$ catalyst by the molecular-beam method[77]. It was found that $TiCl_3$, which does not usually act as a catalyst in the polymerisation of vinyl compounds, on being dispersed in polystyrene rapidly initiates polymerisation to form a non-stereoregular polymer. In a joint condensation of molecular beams of styrene, $TiCl_3$, $(C_2H_5)_3Al$ and solvent rapid non-stereospecific polymerisation occurs, as it does also in the absence of $(C_2H_5)_3Al$. This, evidently, is explained by the high rate of polymerisation of styrene by $TiCl_3$ which exceeds the rate of formation of the catalyst complex $TiCl_3 + (C_2H_5)_3Al$. The authors of this work presume that the polymerisation rate with these complexes is very small at low temperatures. Slow stereospecific polymerisation of styrene takes place only when the monomer is introduced into the reaction after the formation of $TiCl_3$ crystals. The low-temperature polymerisation of styrene with the $(C_2H_5)_3Al + TiCl_4$ catalyst system was also studied by means of an original method, developed by Kabanov *et al.*[77], based on microscopic observation of the polymerisation process in a glass capillary. It was shown that stereospecific polymerisation was possible only when interaction between $(C_2H_5)_3Al$ and $TiCl_4$, with the formation and crystallisation of $TiCl_3$, occurred in the absence of the monomer. When the $TiCl_3$ crystals are formed, it loses the power of initiating rapid non-stereospecific polymerisation.

The role of crystal defects in the initiation of polymerisation was observed in the polymerisation of crystalline acrylate salts and methacrylic acid[78]. In the study of the sodium acrylate–LiCl and sodium acrylate–$MgCl_2$ systems, it was found that rapid polymerisation of the acrylate began on adding just enough of a 50% aqueous C_2H_5OH solution to wet the crystals. In this case the process of polymerisation depends on a heterogeneous exchange reaction between the salts which takes place the moment the mixture is moistened. As a result of this reaction a new crystalline phase (NaCl) emerges and forms nonequilibrium crystallisation catalysts with the crystals of the monomer salt. In the opinion of the authors, defects in the crystal structure, forming at the points of contact, serve as the centres of initiation, for example, "excess" ions stuck in the monomer lattice.

Effective initiation of the polymerisation of crystalline acrylates and methacrylates also occurs on mechanical dispersion of these salts, when defects in the monomer structure are created.

A whole series of monomers (styrene, methyl methacrylate) were polymerised when subjected to intense mechanical grinding with inorganic substances (quartz, graphite, sodium chloride), which in the ordinary state are not polymerisation catalysts[79]. In mechanical dispersion, continuous splitting of particles of the crushed substance takes place with the formation of new solid surfaces which in the first moment are free of adsorbed layers and by virtue of this possess considerable reactivity.

It is interesting that in the grinding of quartz, not only initiation of polymerisation takes place but also chemical grafting of the polymer being formed to SiO_2. This is not difficult to imagine, if it is borne in mind that in the dispersion of the quartz, radicals of the type Si–O– or Si– emerge and introduction of the inorganic substance into the polymer may occur.

The authors think that the mechanism of polymerisation on the exposed solid surface of the inorganic substance depends on the nature of the chemical bonds in the dispersed material and on the nature of the monomer. Thus the polymerisation of styrene by crushed NaCl evidently has ionic character and the polymerisation of styrene by quartz takes place with the participation of free radicals (the existence of free radicals during the dispersion of quartz has been shown experimentally).

In every case where dispersed inorganic substances were used as polymerisation initiators, the polymers

formed had comparatively low molecular weights (of the order of 20 000–30 000). In the authors' opinion this is due to the fact that the concentration of active centres, initiating polymerisation, is rather high. As a result of this, the role of the recombination and disproportionation of the growing polymer radicals increases sharply. Another reason is that polymerisation is accompanied by destruction of the polymer chains.

The experimental data discussed in this paper and the theories evolved from them show, on the one hand, that full use has not yet been made of the possibilities of complex organometallic catalysts in polymerisation, and on the other hand, the large number of unsolved problems connected with the mechanism of stereospecific polymerisation. It is to be hoped that in the next few years we shall see new advances in the application of complex catalysts to the polymerisation of unsaturated compounds of different classes and structure.

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METHODS OF PREPARATION AND PROPERTIES OF SUBSTITUTED VINYL ETHERS AND SULPHIDES

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INTRODUCTION

From the 'thirties onwards a large number of papers were published on the methods of preparation and the reactions of vinyl ethers[1-3], which, by virtue of their high chemical reactivity, have been used extensively in organic syntheses. Vinyl ethers[1-3] and vinyl sulphides[4,5] became easily accessible, especially after the industrial application of the Favorskii–Shostakovskii method of preparation:

$$CH{\equiv}CH+RXH \xrightarrow{\Delta,\ KOH} CH_2{=}CHXR,$$

where X = O, S, N, Si; R = alkyl, aryl.

With the growth in the industrial production of acetylene homologues, there is now a possibility of the latter being applied in the synthesis of substituted vinyl compounds.

Unlike unsubstituted vinyl ethers and vinyl sulphides, substituted ethers and sulphides of the general formula

$$R^1{-}\underset{\displaystyle R^2}{\underset{|}{C}}{=}\underset{\displaystyle R^3}{\underset{|}{C}}{-}X,$$

where R, R^1, R^2, R^3 = alkyl, aryl, halogen, and X = O, S, cannot easily be obtained and as a result are little known. Substituted vinyl ethers and sulphides are of considerable interest in preparative organic chemistry. Like their unsubstituted analogues[2,3], they can, in the presence of acid catalysts, add on a compound containing a mobile hydrogen atom; in this reaction the nature of the substituent has a considerable effect on the rate, yield, and stability of the product. Besides additions to the double bond, they are capable of a number of reactions which are brought about by the presence in the molecule of another reactive centre, such as an alkoxy or mercapto group, or a halogen atom.

The present review deals with the methods of preparation and the basic reactions of substituted vinyl ethers and sulphides and compares them with the like reactions of their unsubstituted analogues. For convenience, the reactions of ethers and sulphides are treated in separate sections.

The review does not cover diene ethers, which can be considered as substituted vinyl ethers containing unsaturated radicals R^1 or R^3, whose double bond is conjugated with that of the vinyl group. Methods of preparation of diene ethers were reviewed by Petrov[6] and Nazarov *et al.*[7]

I. PREPARATION OF SUBSTITUTED VINYL ETHERS

1. Preparation from α-Haloalkenes

Substituted vinyl ethers were first obtained by Butlerov[8] and El'tekov[9] by the reaction of alkenyl bromides with sodium alcoholates. In 1870 Butlerov synthesised β,β'-dimethylvinyl ethyl ether by the following reaction:

$$(CH_3)_2C{=}CHBr+C_2H_5ONa \rightarrow (CH_3)_2C{=}CHOC_2H_5.$$

This method[1-3] has found wide application in the synthesis of unsubstituted vinyl ethers from vinyl chloride. It is of limited value in the synthesis of alkyl-substituted ethers, owing to difficulties involved in the preparation of the starting α-haloalkenes. So far only a few papers have been published on the preparation of alkyl(aryl)-substituted ethers by this method[8-16]. Of note is the work of Niederl