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Three-component Complex Organometallic Catalysts

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The review deals with the literature and patent publications on the polymerisation of olefinic hydrocarbons and some of their derivatives. The mechanism of the action and the specificity of catalytic systems containing mainly ethers and amines are discussed. A small section dealing with systems based on the ether complexes of aluminium alkyls is included. The bibliography includes 236 references.

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I. INTRODUCTION

Catalytic systems based on organometallic compounds (and among them the Ziegler–Natta catalysts) have found wide application in the polymerisation of olefinic and diene hydrocarbons. Together with a high activity, these catalysts in many cases exhibit the so called stereospecificity, i.e. polymers with a definite microstructure (isotactic, syndiotactic, and *cis*- and *trans*-isomeric structures) are obtained in their presence. In order to enhance the specificity of the action of Ziegler–Natta catalysts, i.e. in order to increase the yield of structures which have the most valuable physical and mechanical properties in practice, a number of three-component catalysts have been proposed.

By introducing a third component, the molecular weight of the polymer is regulated and one attains increased rates of polymerisation and an improvement in heat exchange, the sticking of the polymer to the reactor walls, the shaft, and the blades of the stirrer is eliminated, and less dangerous components can be employed[1-9]. The third component increases the selectivity of the catalytic system in the dimerisation of α-olefins[10-12] and the cyclo-oligomerisation of dienes[13,14]. Moreover, the modified systems may prove to be the most suitable for the polymerisation of monomers containing a heteroatom in the substituent[8]. Finally, the modification of Ziegler catalysts is one of the methods helping to elucidate the details of the mechanism and nature of stereospecific polymerisation.

Certain problems associated with the effect of the modification of organometallic catalysts by various compounds[9,15-24], including nucleophilic[25-36] and electrophilic[9,29] substances and aromatic hydrocarbons[29,34,37], and also with the application of complexes of these compounds with one of the components of the catalytic system[28,38-43], have been described in the literature. Data are also available on the effect of admixtures in the catalyst, solvent, and the monomer on the polymerisation process[9,44-52]. However, the extensive experimental data accumulated hitherto have not been described systematically in the review literature and we therefore attempted to fill this gap. The present review deals with systems containing organic compounds as the third component.

2. POLYMERISATION OF α-OLEFINS

In the polymerisation of α-olefins, electron-donating compounds have found the widest application as modifying additives: ethers[1-4,53-59], esters[59-61], amines[62-66], sulphides[67,68], phosphines[69], and certain other O-, N-, S-, and P-containing compounds[70-80]. Solvents or their mixtures are frequently employed for this purpose[9,81]; particular mention should be made of the use of non-fractionated hydrocarbons as solvents[5].

The published data indicate the complex nature of the effect of additives both on the activity and the stereospecificity of the catalyst and on the molecular weight of the resulting polymers[33,35,82-85]. Investigators have frequently approached the consideration of the mechanism of the action of additives from different standpoints and contradictory views exist[25,34,39,86]. The contradictions are aggravated also by the fact that the estimation of the effect of the modification is not made under identical experimental conditions (different amounts of the additive, different order of introduction of the components, etc.).

Razuvaev and coworkers showed that, in the polymerisation of propene in the presence of the $TiCl_3-Al(C_2H_5)_3$ catalyst, the amount of additives introduced has a significant influence on the activity of the catalyst and the molecular weight of the polymer[29,37,86-88]. It has been found[87] that, for the ratio Al : Ti = 3 : 1, an increase in the ratio amine : $TiCl_3$ to 1 entails a sharp increase (by a factor of 2–3) of the molecular weight of the polymer (while the yield remains as usual). These results led the authors to the conclusion that the complexes formed prevent chain termination but do not affect the chain propagation stage. The decrease of the molecular weight of the polymer and its yield observed on increasing the amine : $TiCl_3$ ratio above the equimolar value is accounted for by the binding of the excess amine by $Al(C_2H_5)_3$. An appreciable effect of the order of introduction of the components on the experimental results was not observed. The effect of dioxan, diphenyl sulphide, and pyridine, the amounts of which were varied in the range of the ratio additive : $TiCl_3$ between zero and unity, is fully analogous to the effect of amines but in the presence of dioxan and pyridine there was an appreciable increase in the rate of the process[86].

Under these conditions, the stereospecificity of the catalyst changed insignificantly.

The addition of aromatic hydrocarbons with electron-donating properties[89] has an effect which does not differ in principle from that of other nucleophilic compounds[29,37]. Small amounts of aromatic compounds (benzene, naphthalene, anthracene, diphenyl, styrene) accelerate the polymerisation of propene, while large amounts inhibit it. The compounds can be arranged in the following series in terms of their promoting effect:

benzene ≃ toluene < ethylbenzene ~ isopropylbenzene < *o*-xylene < styrene < tetrahydronaphthalene < mesitylene < anthracene,

which agrees with their sequence in terms of decreasing ionisation potential[37].

Unsaturated aliphatic and alicyclic hydrocarbon can also serve as activators[90-94], but dienes frequently behave as effective polymerisation inhibitors[93,94]. Medvedev and coworkers[93] established that unsaturated compounds can be arranged in the following series in terms of their capacity to reduce the rate of polymerisation of ethylene:

butadiene > isoprene > styrene, isobutene > α-methylstyrene

Minsker[95] explains the effect of the modification of Ziegler–Natta catalysts by a number of polar compounds (amines, ethers, sulphides) in the following way. The reacting monomer molecules are subjected simultaneously to the action of two components of opposed types—the electron-donating ($TiCl_3$) and electron-accepting (AlR_3) components. Therefore, with increase in the amount of the additive, the rate-limiting role may pass from one stage to another (for example, from the electron-accepting to the electron-donating stage and conversely). As a result the additive can behave as a promoting agent at one concentration and as an inhibitor at another.

Vesely[96] found that tributylamine increases the molecular weight of the polymer but does not affect the rate of polymerisation of propene in the presence of the $TiCl_3$–$Al(C_2H_5)_3$ system. In this case the effect of the amine is due to its adsorption on the catalytic centres. As a result of this, the protected active centre cannot be reactivated by extraneous compounds (impurities, the solvent). A number of O-, N-, and S-containing compounds have been investigated in an analogous process[97]. It was found that, when the donor forms a stable complex with AlR_3, the decrease of the concentration of AlR_3, which is capable of giving rise to an active centre on the surface, may be inferred from the decrease of the rate of polymerisation. At a high concentration of the aluminium alkyl small amounts of electron donors increase the rate of polymerisation, while at a low concentration they decrease it. The effect of additives depends on the order of addition of the catalyst components.

Subsequently Ambrož and Hamřik[94,98] reported that electron donors capable of forming 'onium salts behave as promoting agents for catalysts with a low specific surface. For example, tributylamine increased the rate of polymerisation of propene by a factor of 2. At the same time there was an increase in the fraction of isotactic polypropylene and the yield of the amorphous fraction fell. In addition, Kodama and Atarasi[8] observed an increase of the melting point and the density of the polypropylene obtained using the $TiCl_3$–$Al(C_2H_5)_3$–ether (amine) system compared with the polymer synthesised in the presence of the two-component system. The promoting effect of the substances which they investigated varied as a function of their amount, passing through a maximum in all cases.

In order to elucidate the effect of amines in polymerisation on the $TiCl_3$–aluminium alkyl system, Milovskaya and Dolgopol'skaya[99] investigated the distribution of triethylamine between the principal components of the catalyst in the absence of the monomer. It was established that the organoaluminium compound in the complex with the amine is inactive in the polymerisation reaction. When all the components are introduced simultaneously, the amine reacts preferentially with the aluminium alkyl and not with $TiCl_3$. The authors believe that the increase of the molecular weight of the polymer in the presence of amines is due to the formation of a stable complex with the primary aluminium alkyl present in the solution and capable of displacing the polymer chain from the catalytic surface. A similar explanation of the decrease of the activity and the increase of the stereospecificity of the $TiCl_3$–$Al(C_2H_5)_3$ catalyst in the presence of $SeOCl_2$ was put forward by Soga et al.[100]

The mechanism of the action of electron-donating compounds was treated in a different way by Pirogov and Chirkov[39], who assumed that $TiCl_3$ is a fairly strong aprotic acid participating in the double composition reaction

$$TiCl_3 + AlR_3 \cdot D \rightleftarrows TiCl_3 \cdot D + AlR_3 .$$

According to the authors, three-component systems contain not less than five compounds: $TiCl_3$, AlR_3, $TiCl_3$.D, AlR_3.D, and D, their relative amounts varying during the experiment and affecting the activity and the stereospecificity of the catalyst. The activation energy for modified systems is higher than for the $TiCl_3$–AlR_3 two-component system: the values of E_{act} (in kcal mole^{-1}) are 14 for the addition of ether, 19.5 for diphenylamine, 20 for pyridine, and 23 for diethylamine, while in the absence of additives E_{act} is 11.6 kcal mole^{-1}. Thus E_{act} increases with the basicity of the donor. If both compounds are employed as complexes with a Lewis base, the systems are inactive.

The findings of Pirogov and Chirkov are confirmed by other results[28,101]. The occurrence of the reaction involving the exchange coordination of the aluminium alkyl to the donor is proved, according to Pomogailo, Matkovskii, and coworkers, by the fact that the system $VCl_4.2C_5H_5N$–$(iso\text{-}C_4H_9)_2AlCl$ is more active than $VCl_4.2C_5H_5N$–$Al(iso\text{-}C_4H_9)_3$. Since the stability of the complexes of the same ligand is determined by the strength of the Lewis acid, which for organoaluminium compounds varies in the series[102]

$$AlR_3 < R_2AlCl < RAlCl_2 < AlCl_3,$$

it follows that, in the displacement of free VCl_4 from the complex $VCl_4.2C_5H_5N$, di-isobutylaluminium chloride has proved more active than tri-isobutylaluminium.

The authors explain the greater stability of the three-component systems with respect to time compared to two-component systems by the coordination of the amine to the aluminium alkyl. The latter is also a factor which increases the molecular weight of polyethylene.

The studies by Boor[34,82,103,104] on the effect of amines on the polymerisation of propene under the influence of the Ziegler–Natta catalyst and $TiCl_3$–$Zn(C_2H_5)_2$ merits serious attention. The author attributes the fundamental role in the stereospecificity of the catalyst to the nature of the surface of the heterogeneous phase. It is suggested that the active centres are "exposed" titanium atoms and that on the $TiCl_3$ surface isolated centres of various stereospecificities exist. The latter is due to the different ways in which chlorine atoms surround the titanium atoms located in different parts of the crystal (at the corners, on the edges, and on the faces). This imparts to the centres

different capacities for coordinating α-olefin molecules. On the basis of experimental data [82,104], the effect of triethylamine on the rate of polymerisation, the isotactic properties, and the molecular weight of the polymer can be represented schematically in the following way (Fig. 1).

In the region *A* the growth of stereospecificity and the decrease of conversion are due to the binding of non-stereospecific centres, which are most exposed and accessible and also the most "acidic"; in the region *B* the constancy of the stereospecificity and the increase of the conversion are due to the increase of the activity of the remaining more stereospecific centres following the adsorption of the amine next to them (at a chlorine atom); in the region *C*, at high amine concentrations, the constancy of the stereospecificity and the decrease of conversion are caused by the deactivation of the stereospecific centres.

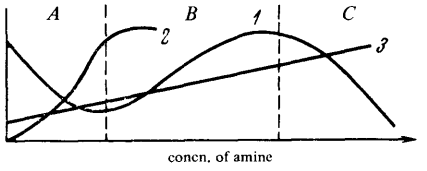


Figure 1. Variation of the degree of conversion (1), the stereospecificity of the catalyst (2), and the molecular weight of polypropylene (3) with the concentration of the amine.

Boor [34,103] divides electron-donating substances into two groups in terms of the nature of their influence. The first group combines substances which decrease the number of active centres as a result of coordination to "exposed" titanium atoms. They always increase the degree of crystallinity, the precise increase depending on the nature of the donor (Lewis bases, azulenes, aromatic compounds and olefins) and its concentration. The second group includes compounds which lower the conversion at low concentrations in consequence of the binding of the active centres and at high concentrations activate the centres (certain aliphatic and heterocyclic amines, phosphines, and azulenes). The results of thermometric titration of catalytic systems by electron donors show that, with substances of the first group, heat is not evolved while in the presence of substances of the second group the heat (exothermic) corresponds to the effectiveness of the donor as an activator of polymerisation. It must be emphasised that Boor believes that the mechanism of the activation process involves the adsorption of the amines on the surface chlorine atoms and not titanium atoms, the main role being attributed in fact to adsorption and not to coordination, since amines with large molecules (tri-n-octylamine) also activate the catalyst, i.e. the steric factor is not very important.

It has been shown in a number of studies [32,105-110] that the two-component system $TiCl_3-C_2H_5AlX_2$, which is inactive in the polymerisation of propene, becomes stereospecific following the introduction of electron-donating additives [111]. Amines, amides, ethers, 'onium salts, phosphines, and sulphides have been investigated as active additives [32,105,110]. Using *NNN'N'N"N"*-hexamethylphosphoramide (HMPA), Coover [110] showed that the rate of polymerisation of propene and the stereospecificity of the catalyst are a maximum when the HMPA: $C_2H_5AlX_2$ ratio is 0.6–0.7. Polymerisation does not occur both in the absence of HMPA and when it is present in excess of the equimolar amount. The same type of behaviour is characteristic of all strong bases, while in the case of weak bases the system is active whatever the amount of the electron donor [109].

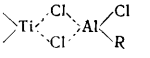
According to the literature [105,108,109,111,112], the stereospecificity of the $TiCl_3-C_2H_5AlX_2-D$ system is analogous to the stereospecificity of the $TiCl_3-(C_2H_5)_2AlX$ system. These results are due to the disproportionation (dismutation) reaction of $C_2H_5AlX_2$ in the presence of Lewis bases with formation of free $(C_2H_5)_2AlX$, which gives rise to active centres:

$$2RAlX_2 + D \rightarrow R_2AlX + AlX_3 \cdot D.$$

The occurrence of this reaction has been confirmed by cryoscopic measurements and the isolation of R_2AlX from the reaction products [108]. Ikegami et al. [113], who investigated the reaction of $(C_2H_5)_3Al_2Cl_3$ [i.e. of $(C_2H_5)_2AlCl$ and $C_2H_5AlCl_2$] with an electron donor (pyridine and dibutyl ether) and also the polymerisation of propene on $TiCl_3-(C_2H_5)_3Al_2Cl_3-D$, arrived at the same conclusion.

However, Coover [32] pointed out that the mechanism of the formation of active centres is more complex than the one discussed above and cannot be reduced solely to the reactions of the individual components. He quotes experimental data in support of this assertion [33]. Thus many compounds with high complex-forming capacity (dioxan and tetrahydrofuran) are ineffective in the polymerisation of propene when combined with $TiCl_3$ and $RAlX_2$. Infrared spectroscopy failed to reveal appreciable amounts of $(C_2H_5)_2AlCl$ in benzene solutions of $C_2H_5AlCl_2$ and HMPA.

It is believed [110] that the donor forms a complex with alkylaluminium dihalide of a type such that the active centre contains a hydrocarbon bridge. On the other hand, in the absence of a third component a dimeric structure with a halide bridge is produced:



It is noteworthy that the system β-$TiCl_3-C_2H_5AlCl_2-$HMPA is more stereospecific than the systems β-$TiCl_3-Al(C_2H_5)_3$ and β-$TiCl_3-(C_2H_5)_2AlCl$. [32,114] With increase of the stereospecificity of the catalyst, the molecular weight distribution of the polypropylene becomes narrower. In general the third component in many cases promotes a narrower molecular weight distribution [114-116].

In contrast to $TiCl_3-AlR_3-D$ systems, the activity of which increases with the basicity of the donor [$C_5H_5N > N(CH_3)_3 > N(C_2H_5)_3$], in systems with $RAlX_2$ the opposite relation is observed [32,107]: the activity of the catalytic system decreases in the series

$$N(C_4H_9)_3 > [N(CH_3)_2]_3PO \sim P(C_4H_9)_3 > (C_4H_9)_2O > (C_4H_9)_2S > C_4H_9I.$$

In a later study [98] other results were obtained for the system $TiCl_4-Al(C_2H_5)_3$, indicating the absence of a direct relation between the electron-donating properties of the additives and their effect on the polymerisation of propenes. In the presence of the system $TiCl_3-(C_2H_5)_3 \cdot Al_2Cl_3$–ether (amine), with increase of the chain length in the ether group the rate of polymerisation of propene increases, the molecular weight of the polymer rises

somewhat, and the stereospecificity of the catalyst falls[57]. The system $VCl_4-(C_2H_5)_2AlCl$ is also sensitive to the effect of the donating capacity of the Lewis base, the activity and stereospecificity of the system increasing as the strength of the Lewis base diminishes[117].

The favourable effect of Lewis bases is attributed to their capacity to increase the degree of dissociation of associated aluminium alkyls[102], which promotes the formation of active centres[107,112,118,119].

In the polymerisation of ethylene in the presence of the system $TiCl_4-LiC_4H_9$–phenetole, it was found[120] that the yield–phenetole concentration and molecular weight–phenetole concentration curves have maxima at a phenetole : Li ratio of unity. Since the above relations show a parallel variation, it was concluded that the lifetime of active centres increases while their number remains constant. An analogous observation was made for the system $VCl_4.2VP-(C_4H_9)_2AlCl-SnCl_4$ (VP = 2-vinylpyridine): the change in the rate of polymerisation and correspondingly of the molecular weight also indicates an increase of the polymerisation rate constant or the lifetime of the catalytic centre[121].

Schindler[122] established different effects of electron donors as a function of the initial ratio of the principal components of the $TiCl_4-(C_2H_5)_2AlCl-D$ catalyst. For the system with Al : Ti = 1.5, an increase of the concentration of D leads only to deactivation, while for the system with Al : Ti = 5 deactivation is observed at low donor concentration, but at high concentration the activity increases. These results are explained by invoking the existence of centres with different activities and containing Ti^{3+} and Ti^{4+}. Deactivation takes place as a result of the binding of the more acidic centres containing Ti^{4+}. According to Schindler, the increase of activity is not caused by the binding of the aluminium alkyl but by the coordination of the donor to the centre containing Ti^{3+}, as in Boor's hypotheses[103].

Table 1. Effect of the order of introduction of the components on the activity of the catalyst.

Order of addition	Monomer	Yield of polymer, g	References
$TiCl_3$—$Al(C_2H_5)_3$	propene	170*	125
$Al(C_2H_5)_3$-pyridine-$TiCl_3$	ditto	172*	125
$TiCl_3$-pyridine-$Al(C_2H_5)_3$	»	250*	125
$TiCl_4$—LiC_4H_9	ethylene	4.00	120
$TiCl_4$-phenetole-LiC_4H_9	ditto	5.25	120
LiC_4H_9—$TiCl_4$	»	1.10	120
LiC_4H_9-phenetole-$TiCl_4$	»	3.50	120
Pyridine-VCl_4-anisole-(iso-$C_4H_9)_2AlCl$	propene	0.00	117
Anisole-VCl_4-(iso-$C_4H_9)_2AlCl$-pyridine	ditto	0.9	117

*The yield is given in grammes per gramme of catalyst.

The activity of catalytic systems depends on the order of introduction of the components[117,120,123]. When anisole is added to the product of the reaction of VCl_4 and R_2AlCl, a catalyst with a lower stereospecificity is formed than following the addition of R_2AlCl to VCl_4 + anisole or of VCl_4 to R_2AlCl + anisole[117]. These results suggest that the electron donors are active components of the catalyst.

A number of workers established experimentally that it is best to introduce the catalyst components in the following sequence: the transition metal compound, the donor, and the metal alkyl (Table 1).

Having investigated the polymerisation of propene in the presence of the system $VCl_4-(C_2H_5)_2AlCl-D$, Natta et al.[124] arrived at the conclusion that the effect of anisole, the most effective of all the donors investigated (anisole, furan, isopropyl ether, diethyl ether, thiophen, pyridine, and triethylamine), is associated with its coordination both to the transition metal compound and to the organometallic compound:

$$VCl_4 + D \rightarrow VCl_4 \cdot D,$$
$$2\,(C_2H_5)_2AlCl + 2D \rightleftarrows 2\,(C_2H_5)_2AlCl \cdot D.$$

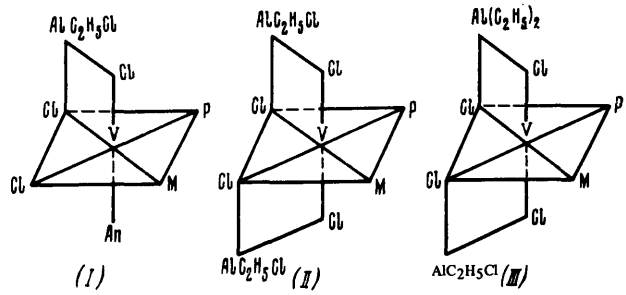


Figure 2. The structure of stereospecifically active vanadium(III) complexes in the presence (I) and absence (II and III) of anisole; P—growing molecule; M—complexed monomer; An—molecule of anisole or another Lewis base[124].

It is assumed that only free $(C_2H_5)_2AlCl$ is capable of alkylating VCl_4 or $VCl_4.D$. The catalytically active vanadium compound is formed by the reaction

$$(C_2H_5)_2VCl_2 \rightarrow C_2H_5VCl_2 + C_2H_5^{\cdot} \quad \text{or} \quad (C_2H_5)_2VCl_2 \cdot D \rightarrow C_2H_5VCl_2 \cdot D + C_2H_5^{\cdot}.$$

Complexes of six-coordinate V^{3+}, constituting one of the structures presented in Fig. 2, are suggested as stereospecifically active centres.

3. POLYMERISATION OF DIENE HYDROCARBONS

The polymerisation of diene hydrocarbons in the presence of Ziegler catalysts using electron-donating additives (amines, ethers, thiophen, etc.) has been described in a number of patents[126–142]. Thus it has been suggested that butadiene be polymerised at 10–50° with a $TiCl_3I-AlR_3-D$ catalyst, whereby it is possible to obtain polymers containing more than 80% of *cis*-1,4-units. The molar ratio of the catalyst components is 1 : 1.5 : 1.5.[137] As with α-olefins, the introduction of an electron donor accelerates the polymerisation[133], and regulates the molecular weight[138]. In many cases the content of the gel fraction and of cyclisation products is reduced[143]. When three-component systems are employed, the preferential formation of *cis*-1,4-,[132,139] *trans*-1,4-[138] or 1,2-structures[129,130] is achieved.

Following the introduction of ethers into the $TiI_4-Al(iso\text{-}C_4H_9)_3$ system, Dolgoplosk and coworkers[144] observed a change in the polymer microstructure: a decrease of the content of *cis*-1,4-units and hence an increase of the content of *trans*-1,4-units; the content of

1,2-units remained constant. The ethers can be arranged in the following series in terms of their effect:

dimethyl ether > ethyl methyl ether > diethyl ether > dibutyl ether,

i.e. the effect of the ether decreases with increase in the length of the hydrocarbon group and follows the decrease of the tendency towards complex formation. Therefore, in order to obtain a polymer with a high content of *cis*-1,4-units, one adds di-isopropyl ether [83,140], the electron-donating capacity of which is probably reduced owing to the steric factor. It has been noted that in the presence of electron donors the molecular weight of the polymers falls [145]. The introduction of an excess of dimethyl ether in relation to the aluminium alkyl causes a complete reversal of the microstructure with formation of a crystalline *trans*-1,4-polymer [23].

The effectiveness of sulphides as well as ethers decreases with increase in the length of the hydrocarbon group: $(C_2H_5)_2S > (C_4H_9)_2S > (C_8H_{17})_2S$. Tetrahydrofuran has a powerful effect [146]. Only compounds with a greatly reduced activity (thiophen, diphenyl sulphide, and diphenyl ether) have no influence on the chain microstructure and the polymerisation kinetics.

It is noteworthy that, when the polymerisation of isoprene is performed in diethyl ether, dioxan, aniline, dimethylaniline, and pyridine, a polymer is not formed [147]. However, in di-isopropyl ether there is a possibility of the formation of *cis*-1,4-polybutadiene [141].

The system comprising $TiCl_4$, AlI_3, and $AlHCl_2$ leads to *cis*-1,4-polybutadiene when it contains an ether or an amine in an amount equimolar with that of $AlHCl_2$. With increase of the amount of the electron donor, the content of the *trans*-units rises owing to a decrease from the content of the *cis*-units, i.e. the additives have the same effect as in the TiI_4-AlR_3 system. Analogous results were obtained in the polymerisation of isoprene under the influence of $TiCl_4-AlHCl_2.O(C_2H_5)_2$. Systems containing trimethylamine exhibit high stereospecificity [23].

The introduction of β-naphthylphenylamine into the $TiCl_4-Al(C_2H_5)_3$ system makes it possible to obtain polyisoprene not containing a gel [118]. The rate of polymerisation and the degree of conversion depend in this case on the order of introduction of the catalyst components.

The simultaneous addition of two donors (an ether and an amine) is interesting [148]. The introduction of an amine into the polymerisation system together with an ether leads in some cases to a considerable acceleration of the process. At the same time the content of the gel diminishes but the molecular weight and the polymer structure remain constant. The presence of an amine and an ether makes it possible to alter the relative amounts of the principal catalyst components without risk of increasing the content of the gel or of retarding the polymerisation.

Systems consisting of $CoCl_2$ complexes with pyridine or an alcohol in combination with R_2AlCl exhibit high stereospecificity [149-152]. It has been established that the addition of ethers, amines, and sulphides to a cobalt catalyst leads to a sharp change in the structure of the polydiene chain and a decrease of the rate of polymerisation and the molecular weight of the polymer [145]. The addition of AlR_3 has a similar influence [153-155]. The opposite effect is obtained in those cases where small amounts of water, alcohols, $AlCl_3$, $RAlCl_2$, Br_2, and other compounds are introduced [155-157]. It has been shown [154] that the complex formed from cobalt halides and $(C_2H_5)_2AlCl$ is active. There is then no oxidation-reduction interaction between the catalyst components. On the other hand, in the presence of AlR_3 cobalt is reduced to the metal with simultaneous formation of R_2AlCl and other substances. The above negative effects are associated with this reduction. In a treatment from a single standpoint of all these phenomena, Vinogradov, Dolgoplosk, and coworkers [158] start from the known fact that R_2AlCl solutions form AlR_3 under the influence of electron donors. Thus the effect of donors is analogous to that of AlR_3 additives.

On the other hand, when catalytic systems based on $CoCl_2-RAlCl_2$ [108,109,159] and $CoCl_2-AlCl_3$ [160] are employed, small amounts of donors are essential for the preparation of the *cis*-polymer, since in this case Lewis bases bind free $AlCl_3$ and suppress cationic polymerisation. Judging from the change in the degree of unsaturation of the polymer, anisole and thiophen are the most effective. Nitrogen-containing compounds (pyridine, diphenylamine, dimethylaniline) proved to be unduly powerful donors for this system; they break down the catalytic complex with formation of $CoCl_2$.

Electron-donating additives have the same influence on the homogeneous $CoCl_2.2D-(C_2H_5)_2AlCl$ system (D = pyridine or acetylacetone) [36,161] as on the heterogeneous system [145]. However, in the case of the homogeneous system the observed decrease of the molecular weight of the polymer is associated with the participation of free donors in the chain-transfer reaction [161]. This view is confirmed by the fact that an increase of the concentration of the aluminium alkyl leads to an increase of both the degree of polymerisation and the catalyst activity. An increase of the concentration of the aluminium component should lead to a decrease of the concentration of the free Lewis base. If at the same time there is an increase of the molecular weight, it follows that it is in fact the free donors which influence the chain growth limitation reaction. As already mentioned [162], the $R_2AlCl-CoCl_2.2C_5H_5N$ system is active in the preparation of the *cis*-1,4-polymer of butadiene only in the presence of water or other electron-accepting substances.

The most complete data on the kinetics of this reaction have been presented by Karchevskaya et al. [163] Water not only accelerates the polymerisation and increases the molecular weight but, after the attainment of the optimum concentration, the excess water breaks down the active centres and reduces the rate of polymerisation, but the molecular weight continues to grow. This complex effect of water is due to its dual nature, i.e. its electron-accepting and electron-donating properties.

Kinetic data for the systems $CoCl_2.2C_5H_5N-(C_2H_5)_2.AlCl-A$ (A = $AlCl_3$, $SnCl_4$, or $C_2H_5AlCl_2$) have been presented [164]. When $C_2H_5AlCl_2$ is introduced, the rate of polymerisation increases and reaches a maximum for the equimolar $(C_2H_5)_2AlCl : C_2H_5AlCl_2$ ratio. Further increase of the amount of $C_2H_5AlCl_2$ leads to the appearance of an introduction period, which is a maximum in the absence of $(C_2H_5)_2AlCl$. The molecular weight increases continuously with the amount of additive and is a maximum when the aluminium component is completely replaced by $C_2H_5AlCl_2$.

In the absence of additives, the rate of the process is low; only an oligomer was obtained: the authors suggest that the aluminium component participates in the formation of active centres and also in the decomposition of these centres and chain transfer.

Recently it has been established [165,166] that the addition to the catalytic system of halogenohydrocarbons containing two and more halogen atoms (for example CH_2Br_2 and CH_2Cl_2) increases the activity of the catalyst and makes it possible to obtain a high yield of polyisoprene containing 97-98% of *cis*-1,4-units.

4. POLYMERISATION AND COPOLYMERISATION OF OTHER MONOMERS

The effect of a large number of organic compounds containing a heteroatom on the polymerisation of styrene in the presence of $TiCl_4-Al(C_2H_5)_3$ has been investigated. It has been found that only thiophen and furan increase the stereospecificity of the system (the conversion of styrene then diminishes). Many substances (halogenobenzenes, di-n-hexyl ether, and triphenylphosphine) reduce the yield of polystyrene without affecting its structure. On the other hand, most of the compounds eliminate the stereospecificity of the catalyst, diminishing or increasing the conversion of styrene. The effect of additives reduces to binding the substances responsible for non-stereospecific cationic polymerisation. The inhibiting effect of additives is shown particularly clearly at the high concentrations employed in the study quoted above. In the polymerisation of styrene in the presence of β-$TiCl_3-Al(C_2H_5)_3$ and β-$TiCl_3-(C_2H_5)_2AlCl$ an increase of the rate of formation of the isotactic polymer is observed when straight-chain dipropyl, dibutyl, and dihexyl ethers and triethylamine are introduced up to a donor : aluminium component ratio of unity[35]. Further addition of the donor leads to a sharp decrease in the rate of polymerisation.

The effectiveness of the substances investigated decreases in the sequence

$$(n\text{-}C_6H_{13})_2O > (n\text{-}C_4H_9)_2O > (n\text{-}C_3H_7)_2O > (C_2H_5)_3N.$$

In the polymerisation of acetylene under the influence of $TiCl_4-Al(iso\text{-}C_4H_9)_3-D$, the addition of dioxan (0.05–0.1 mole per mole of $TiCl_4$) or triethylamine (0.1–0.3 mole per mole of $TiCl_4$) increases the yield of polyacetylene only when the Al : Ti ratio is less than the optimum value (for the two-component system); in other cases the additives sharply inhibit polymerisation[26].

Catalysts modified by Lewis bases are used for the polymerisation of iodo-derivatives of α-olefins in which the carbon–iodine bond is remote from the double bond[168]. The polymerisation of fluorine-containing monomers[169], symmetrical dichloroethylene[170], and vinylidene chloride[171] in the presence of similar systems has been described.

The introduction of tetrahydrofuran, triethylamine, pyridine, and diethyl ether alters sharply the activity and nature of the $Ti(OC_4H_9)_3-C_2H_5AlCl_2$ catalytic system in the copolymerisation of ethylene with vinyl chloride[172], which is evident from the change in the composition and yield of the copolymer (Table 2). On the other hand, anisole and thiophen do not have a significant influence on the activity of the system, while acetylacetone, triphenylphosphine, and dipyridyl inhibit polymerisation. According to infrared spectroscopic data, the copolymer obtained in the presence of anisole and thiophen is identical with the product synthesised without a donor and is predominantly a block copolymer. On the other hand, the spectra of the copolymers obtained in the presence of tetrahydrofuran, triethylamine, pyridine, and diethyl ether are analogous to the spectrum of the copolymer synthesised in the presence of $B(C_4H_9)_3$–t-butyl peroxide by a radical mechanism[173]. In the absence of tetrahydrofuran the composition of the copolymer is constant and the yield depends on the Al : Ti ratio.

Isotactic and syndiotactic poly(vinyl chloride) is obtained in the presence of the three component system transition metal (Ti, V, Zr, Fe, or Ni) chloride–$Al(C_2H_5)_3$–D.[174–178] In the absence of a Lewis base the polymerisation of vinyl chloride under the influence of $VOCl_3-Al(iso\text{-}C_4H_9)_3$ is slow. In the presence of ethyl acetate effective polymerisation takes place at −30°C. The authors adduce evidence for the suggested radical mechanism for this process[179].

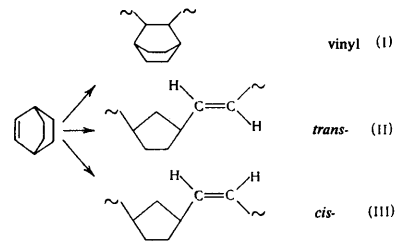
The copolymerisation of ethylene and butadiene[180–182] and ethylene and α-olefins[183–189] in the presence of three-component catalysts has been described. Under these conditions, the third component not only promotes an increased yield but also improves the physical and mechanical properties of the copolymers. The electron-donating component is then introduced as a complex with a transition metal halide[189] and more rarely with an aluminium alkyl[180].

Table 2. Copolymerisation of ethylene with vinyl chloride*.

Donor	Al:Ti	Yield, %	Vinyl chloride in copolymer, mole %	Type of copolymer	$[\eta]$**, dl g^{-1}
—	3.0	20.2	15.8	block	0.42
Tetrahydrofuran	3.0	31.6	86.8	non-regular	0.26
Triethylamine	3.0	24.0	86.1	ditto	0.24
Pyridine	3.0	22.5	89.3	»	0.30
Ether	3.0	11.1	79.5	»	0.26
Anisole	3.0	12.2	20.1	block	0.21
Thiophen	3.0	12.0	13.4	ditto	0.24
Dipyridyl	3.0	1.8	—	—	—
Acetylacetone	3.0	0	—	—	—
Triphenylphosphine	2.2	0	—	—	—

*Experimental conditions: 0.35 mole of ethylene, 0.35 mole of vinyl chloride, and 2.0×10^{-3} mole of $Ti(OC_4H_9)_3$; D : Ti = 1; 50 ml of n-heptane; temperature 50°C; duration of polymerisation 3 h.
**Measured in cyclohexanone solution at 30°C.

Lewis bases alter the mode of polymerisation of norbornene[190,191]. In the presence of the usual Ziegler catalyst norbornene is polymerised at the double bond with *trans*-ring opening, while in the presence of Lewis bases the polymerisation takes place only with *trans*- and *cis*-ring opening:



5. CATALYTIC SYSTEMS BASED ON THE ETHER COMPLEXES OF ORGANOALUMINIUM COMPOUNDS

In many studies it has been suggested that, instead of free aluminium alkyls or the addition of ethers to two-component catalysts, pre-synthesised ether complexes of aluminium alkyls be employed[1,38–42,136,142,192–202]. In some cases this leads to certain advantages; since in contrast to ether-free aluminium alkyls, the ether complexes are more convenient to prepare and handle[203] and can be obtained in the laboratory without particular difficulty[201,204–206].

Moreover, ether complexes in many cases promote the formation of polymers with valuable physical and mechanical properties. However, until recently little attention was devoted to the study of the properties of the ether complexes of organoaluminium compounds as catalysts, since it was believed[207] that ethers forming stable complexes with aluminium compounds deactivate the Ziegler–Natta systems.

The studies were mainly directed to the search for means of separating the ethers from the organometallic component. The results of the measurement of the heat of formation of triethylaluminium-ether complexes[208] suggested that the replacement of diethyl ether by an alkyl aryl ether will yield ether complexes from which ether can be readily eliminated by distillation and which can be employed as active components in catalytic systems by virtue of the presence of weakened Al ← O bonds. An inverse relation was found between the enthalpy of dissociation of the ether complexes and their polymerisation activity with respect to ethylene[41,209]. The catalyst is much less sensitive to the electron-donating capacity of the ether in the polymerisation of propene[34,202]. In this case even adducts of triethylaluminium with diethyl ether[196] and monoglyme[197] exhibit a high activity. Complexes of ethylaluminium dichloride with di-isopropyl, di-n-butyl, and di-isopentyl ethers are effective in the stereospecific polymerisation of propene[210].

It has been reported[42] that polyethylene obtained in the presence of systems with ether complexes is similar in some of its properties to the Ziegler polyethylene and, according to infrared spectroscopic data, does not contain methyl side groups[40,41].

The yield of polyethylene in the presence of the $TiCl_4$–$Al(C_2H_5)_3.C_6H_5OC_2H_5$ catalyst[202] depends on the Al : Ti ratio, but this dependence is not as pronounced as for the ether-free catalyst[211]. It is well known that the activity of the catalyst is higher when it is formed in the presence of the monomer. A similar effect is shown also for ether complexes[202]. In the presence of ether or the monomer, the molecules of which behave as ligands, the following complexes may be formed:

$$[TiCl_3]^+ \xrightarrow{ROR'} [TiCl_3]\ (I) \quad \text{or} \quad [TiCl_3]^+\ (II)$$

(I): the ether oxygen of ROR′ coordinates to the Ti; (II): $CH_2=CH_2$ coordinates to the Ti.

As a result, further reaction between the components of the bimetallic complex $[TiCl_3]^+[Al(C_2H_5)_3Cl]^-$ is hindered, which leads to its deactivation. Then the Ti–C bond in compound (II) should be comparable in strength to the Ti ← O bond in compound (I). For ethylene, this is observed in the case of ethers containing an aryl group (weak nucleophilic agents). Depending on the monomer, different ethers cause deactivation.

Mardykin et al.[212] compared the effectiveness of ether complex systems with ether-free systems in the polymerisation of styrene. The corresponding results are presented in Table 3, from which it follows that the $TiCl_n$–$Al(C_2H_5)_3$.ether systems are active in the stereospecific polymerisation of styrene.

With the aid of the ether complexes of aluminium alkyls optically active poly-α-olefins have been obtained even from optically inactive olefins[217–219].

The ether complexes of aluminium alkyls are also active in the polymerisation of dienes (isoprene, butadiene, etc.), the ether complexes of tri-isobutylaluminium being most often used in such cases. In the presence of systems of this kind polyisoprene with the properties of natural rubber is obtained[142,198–200,220].

The polymerisation of penta-1,3-diene[219], hexa-1,3,5-triene[221], and other conjugated trienes[222] in the presence of ether complexes has been described.

Together with the ether complexes of aluminium alkyls, complexes of organoaluminium compounds with amines have been employed in the polymerisation of olefins[223] and organic sulphide complexes of aluminium alkyls have been employed in the polymerisation of dienes[224].

Table 3. Stereospecificity of the $TiCl_n$–AlR_3 (a) and $TiCl_n$–AlR_3.ether (b) systems in the polymerisation of styrene.

Conversion	Duration of polymerisation, h	Crystallinity, %	Yield of crystalline polymer, %	System	References
		Catalysts with $TiCl_4$			
9	2–6	89	8.0	a	213
5–28	3–4	44–81	0.6–15.6	a	214
13	4	38.8*	4.9	a	167
3	7	50	1.7	a	215
13–100	2–5	1–20	0.9–3.8	b	212
		Catalysts with $TiCl_3$			
71	6.5	94	66.7	a	216
16–66	3–12	85–90	13.3–60	b	212

*Extraction with ethyl methyl ketone and in the remaining cases with acetone.

The copolymerisation of ethylene with nitrogen-containing monomers (acrylonitrile, diallylamine, etc.) previously bound in complexes with one of the components of the Ziegler catalyst is of considerable interest[225,226].

The above review of the applications of three-component systems shows that a positive effect is achieved by introducing into the Ziegler–Natta catalysts substances of different types: ethers, amines, phosphorus derivatives, sulphur derivatives, alcohols, water, salts, etc. Evidently the mechanism of the action of such a wide variety of reagents cannot be common to all of them. Moreover, the role of the third component must be considered in relation to a definite class of substances constituting the basis of the catalytic system. Until recently in the study of three-component systems the principal role was attributed to processes involving the chemisorption of electron-donating compounds on the active centres of the catalyst[29,82]. Admittedly, in most cases the third component was introduced to a complex already formed from the principal components (MX_n–ER_m; M = transition metal, X = halogen, and E = Al, Mg, Li, etc.). In these cases the effect of the donor is shown by virtue of its binding in a complex (or chemisorption on) already existing polymerisation centres.

The third component has a more profound specific effect when it interacts with one of the principal components of the catalyst before the formation of the catalytic complex proper. The complexes of the catalyst components formed under these conditions will behave differently in the chemical reaction and will yield products (some of which are active centres) differing from those obtained when free (non-complexed) components are employed.

Thus, together with chemisorption, in three-component systems account must be taken also of chemical reactions between all three components. One of the principal reactions in the formation of the catalytic complex is the alkylation and reduction of the transition metal compound:

$$AlR_3 + TiCl_4 \rightarrow RTiCl_3 + R_2AlCl;\ RTiCl_3 \rightarrow TiCl_3 + 1/2\,R_{(+H)} + 1/2\,R_{(-H)}.$$

Nucleophilic compounds accelerate this reaction [25,31,38,158]. If the Ti–C bond is assumed to be the active centre [227-231], the increase of the rate of alkylation of titanium will lead to an increase in the number of active centres and a corresponding acceleration of the polymerisation process. The electron donor coordinated to the catalytic complex losens the Ti–C bond by virtue of the increase of the electron density around the titanium atom and thereby facilitates the insertion of the monomer into the active centre [232]. Moreover, as the reaction between the components of the catalytic system proceeds, there is a possibility of the formation of new complexes, since certain reaction products are stronger Lewis bases. For example, in the $TiCl_4-AlR_3$ system these are R_2AlCl, $RAlCl_2$, and $AlCl_3$. As a result, the donor is transferred to the powerful new electron acceptors appearing in the system and new more stable complexes are formed: $R_2AlCl.D$, $RAlCl_2.D$, and $AlCl_3.D$. In turn, these complexes behave differently than the corresponding free compounds. Thus, under certain conditions, the complexes $R_2AlCl.D$ and $RAlCl_2.D$ disproportionate with formation of an additional amount of the initial organometallic component:

$$2R_2AlCl + D \rightarrow AlR_3 + RAlCl_2 \cdot D,$$
$$2RAlCl_2 + D \rightarrow R_2AlCl + AlCl_3 \cdot D \text{ etc.}$$

Consequently in the presence of the donor, the effective concentration of the organometallic component increases which, depending on its initial concentration, determines the effectiveness of the catalytic system. However, not all donors are capable of being transferred from one component to another. Some of these are irreversibly bound in complexes with the initial components and are cleaved:

$$RAlX_2 + R'OR'' \rightarrow RAlX_2 \cdot O\langle^{R'}_{R''} \rightarrow RAlX(OR') + R''X,$$

$$TiCl_4 + R'OR'' \rightarrow TiCl_4 \cdot O\langle^{R'}_{R''} \rightarrow TiCl_3OR' + R''Cl.$$

In the presence of $AlCl_3$ and other Lewis acids alkyl aryl ethers readily rearrange to alkylphenols [233]. Phenol and its alkyl derivatives have been detected [234] among the products of the reaction between $TiCl_4$ and $Al(C_3H_7)_3$. $.C_6H_5OCH_3$.

Electron donors reacting in the above manner deactivate (disrupt) the catalyst when present in equimolar amounts in relation to the main components. Only those donors which are not cleaved or are cleaved only to a slight extent exhibit a positive modification effect when present in large amounts.

In the latter case the degree of reduction of the transition metal and hence the activity of the catalytic system increase owing to the formation of alkoxy-derivatives, since the presence of RO groups in the $TiCl_4-(C_2H_5)_2AlCl$ system in amounts up to 25% greatly increases the degree of reduction of $TiCl_4$. [235] Systems containing alkoxy-derivatives of titanium proved to be more effective. The effect of small amounts of active substances such as alcohols and water should be treated similarly.

The complexity of the relation between the molecular weight of the polymer and the amount of the donor is due to the fact that the donor can (1) behave as a chain-transfer agent, (2) can form complexes with chain-transfer agents, (3) can alter the chain propagation rate constant or the lifetime of the active centre by forming complexes with the latter, and (4) can influence the molecular weight by altering the relative amounts and the activities of the main components.

The differences in the electron-donating capacity and the structure of additives are shown in the fact that they exhibit the same effect at unequal concentrations [236]. As a rule, small amounts of the donor increase and large amounts reduce the molecular weight of the polymer.

The stereospecificity of catalytic systems depends similarly on the content of the electron-donating compound. When a third component is introduced, the number and activity of the stereospecific and non-stereospecific centres change owing to both chemical reactions and adsorption processes.

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