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Hydro-dehydropolymerisation and Isomerisation Polymerisation of Unsaturated Hydrocarbons

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Consideration is given to the effect of hydro-dehydropolymerisation, discovered by S.S.Nametkin and his coworkers in a study of the polymerisation of unsaturated hydrocarbons under the influence of sulphuric acid and aluminium chloride. This phenomenon is significant in the investigation of the oligomerisation and polymerisation of alkenes in the presence of various catalysts. Research on the monomer-isomerisation polymerisation of alkenes is analysed. A list of 53 references is included.

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I. INTRODUCTION

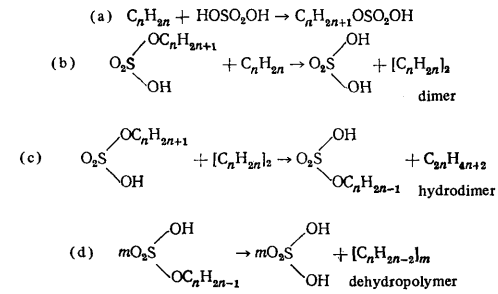
The formation of polymers by the action of sulphuric acid, aluminium chloride, and other acidic reagents on unsaturated hydrocarbons long ago attracted the attention of chemists, from Butlerov to the present time. After only a century many hundreds of papers on aspects of the polymerisation of unsaturated hydrocarbons are published annually in various chemical periodicals. Butlerov himself showed[1] that unsaturated hydrocarbons undergo polymerisation in the presence of sulphuric acid, with the formation of unsaturated compounds of higher molecular weight. The polymerisation of different types of unsaturated hydrocarbons and their derivatives has since been the subject of numerous investigations of various kinds. However, many aspects of the catalytic polymerisation of alkenes, in particular cationic polymerisation, have remained obscure.

Here we cannot consider the whole multiplicity of processes in the polymerisation of alkenes under the influence of acidic catalysts. These problems have been covered in a monograph and many review papers[2-4].

The present issure of Uspekhi Khimii is dedicated to the memory of S. S. Nametkin, whose researches on the reactions of unsaturated hydrocarbons in the presence of sulphuric acid and aluminium chloride led to the discovery of a new reaction, which he termed hydro-dehydropolymerisation. In addition, special attention is paid to monomer-isomerisation polymerisation, as an example of the variety of reactions involved in the polymerisation of alkenes. Nametkin's work on polymerisation resulted also from a non-trivial approach to the peculiarities of a well known chemical reaction.

II. HYDRO-DEHYDROPOLYMERISATION OF ALKENES WITH SULPHURIC ACID AND ALUMINIUM CHLORIDE

In his investigation of the reactions of unsaturated hydrocarbons in the presence of sulphuric acid Nametkin observed[2] the somewhat anomalous simultaneous formation of polymerisation products containing both unsaturated and saturated hydrocarbons[5]. He concluded that this was the result of the concerted occurrence of polymerisation, hydrogenation, and dehydrogenation. Polymers of saturated character, hydropolymers, were formed. The acid polymerisation of unsaturated hydrocarbons can in this case be represented by the general scheme[5]



which was proved correct by examining the composition of intermediate and final products.

A later study in Nametkin's laboratory of certain aspects of the preparation of isopropyl alcohol showed that hydro-dehydropolymerisation takes place in the course of the hydration of propene to propan-2-ol by means of sulphuric acid[6]. Other catalysts also effect hydro-dehydropolymerisation. Nametkin et al.[7] made a detailed study of this process when aluminium chloride acts on unsaturated hydrocarbons, in particular ethylene, pentene, etc. They pointed out that the action of aluminium chloride is complicated by partial degradation of the hydrocarbons. Subsequently Nametkin and his coworkers showed that hydro-dehydropolymerisation is observed with a wide range of unsaturated hydrocarbons of various classes. It was thus demonstrated experimentally[8] that the action of aluminium chloride on cyclohexene yields products whose formation can be explained in terms of this phenomenon. They included[8] two hydrocarbons—an unsaturated pentamer of cyclohexene (tetracyclohexylcyclohexene) and tetracyclohexylbenzene—of relatively high molecular weight. Reporting this extremely curious experimental fact, Nametkin pointed out that "the immediate mechanism of the formation of the aromatic derivative

and equally of the accompanying naphthenes is still not clear, and further research is required to elucidate the routes by which they are formed". The hydropolymerisation of unsaturated hydrocarbons was later studied by Nametkin on 3-methylbut-1-ene treated with sulphuric acid monohydrate[9].

The above results suggest that the new phenomena, discovered by Nametkin and his coworkers in the polymerisation of unsaturated hydrocarbons under the influence of sulphuric acid or aluminium chloride, are general in character. They were of substantial value for the understanding of several complicated reactions involved in the production from unsaturated hydrocarbons of several technically important products (in particular, components of certain lubricating oils).

It must be borne in mind that, when aluminium chloride is used as catalyst, polymerisation is nearly always complicated by degradative effects, leading to the formation among the reaction products of compounds in which the number of carbon atoms is not a multiple of the number in the initial alkene.

A later paper by coworkers of Nametkin showed[10] that cyclopentene undergoes interesting reactions under the influence of aluminium chloride, and established for the first time the formation from cyclopentene of spirodecane. They suggested that the monomer initially dimerises, after which one ring of the dimer expands to a six-membered ring (by incorporating a carbon atom of the second ring). Trimers, tetramers, and hexamers would be formed in the same way. Unfortunately, direct evidence of the hypothetical mechanism could not be supplied at that time. In a systematic survey of several experimental investigations Rudenko[11] stated that the formation of hydropolymers from several alkenes in the presence of aluminium chloride results from a redistribution of hydrogen between the hydrocarbons forming a complex with the catalyst and the polymers. The hydrogen donors are catalytic complexes, which is confirmed experimentally by their highly unsaturated state.

In the above papers Nametkin, having examined critically results published by that time on the polymerisation of unsaturated hydrocarbons, points out that the proposed division of polymerisation processes into thermal and catalytic is incorrect. He considers that the only correct criterion for a classification of the polymerisation reactions undergone by unsaturated hydrocarbons is the composition of the products. He therefore proposes the following classification[5].

1. Polymerisation. The formation from unsaturated hydrocarbons of likewise unsaturated dimers, trimers, etc. had first been observed by Butlerov. Polymerisation may take place either at low temperatures under the influence of various catalysts (dilute sulphuric acid, zinc chloride, etc.) at high pressures and temperatures (thermally or catalytically, in particular in the presence of phosphoric acid).

2. Hydro- and dehydro-polymerisation. This process differs from polymerisation in yielding saturated hydropolymers and simultaneously highly dehydrogenated products from the unsaturated hydrocarbons. Since these products are formed at the same time, the total quantity of hydrogen involved in the reactions can be balanced.

Alkenes of iso-structure exhibit less tendency to hydropolymerisation than do the straight-chain hydrocarbons. Nevertheless, effects due to hydro-dehydropolymerisation must sometimes be reckoned with in such technically important processes as the polymerisation of isobutene. Special additives for synthetic oils are among the important products obtained from isobutene. One of the very first studies in this field, made[12] under Nametkin's direction, established that the polymerisation of isobutene in the presence of aluminium chloride (3%) at low temperatures (−78°C) yields a rubberlike polymer of molecular mass 20 000–30 000, which the authors named "superol". Several methods for obtaining polyisobutene have now found practical application, but their discussion lies outside the scope of the present Review.

Hydro-dehydropolymerisation has since been observed on other catalysts. One of the first monographs on the catalytic polymerisation of alkenes in motor fuel[13] mentions that, in the presence of phosphoric acid at sufficiently high temperatures (up to 300°C), polymerisation is accompanied by hydro-dehydropolymerisation, so that the unsaturated compounds obtained are accompanied by saturated—including cyclic—hydrocarbons.

III. REDISTRIBUTION OF HYDROGEN IN THE REACTIONS OF UNSATURATED HYDROCARBONS ON ALUMINOSILICATE AND OTHER CATALYSTS

During the 1940–1950s the attention of investigators was especially attracted to the reactions of hydrocarbons on aluminosilicate catalysts, which acquired exceptionally important industrial value in the cracking of petroleum products. Such catalysts served and continue to serve as subjects of thousands of publications, which, of course, we do not intend even partly to survey here. The attention of the reader will be directed merely to several studies which definitely established common features in the mechanism of the action of acidic and aluminosilicate catalysts and revealed the occurence of the hydro-dehydropolymerisation of hydrocarbons on the latter.

An example is the investigation of Petrov and Frost[14], planned in some measure as a continuation of the classical studies of Lebedev and his coworkers[15], who were the first to report the redistribution of hydrogen in the transformation of unsaturated hydrocarbons on Floridin (the investigation was made on di-isobutylene and di-isopentylene [*sic*]). Petrov and Frost aimed to study the influence of the structure of the initial hydrocarbon on hydrogen redistribution on an aluminosilicate. They found that the yield of saturated products formed by hydro-dehydropolymerisation in a series of linear alkenes increases with the length of the hydrocarbon chain. This rule does not apply to cycloalkenes.

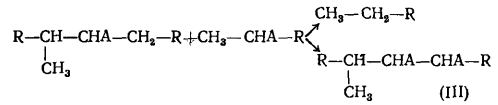
Aluminium silicate can be formulated $(HAlSiO_4)_n$ or in abbreviated form HA (i.e. it is analogous to an inorganic acid), and is able to exchange its hydrogen atoms for those of hydrocarbons reacting with it. Polymerisation (e.g. of hex-1-ene) may then occur as follows:

$$CH_2{=}CHR + HA \rightarrow \underset{(I)}{CH_3CHA{-}R}$$
$$H_3C{-}CHAR + CH_2{=}CH{-}R \rightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CHR + HA\ ,$$

which is fully analogous to Butlerov polymerisation. The dimer then reacts again with the catalyst:

$$R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH{=}CH{-}R + HA \rightarrow R{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CHA{-}CH_2{-}R \quad (II)$$

Interaction between complexes (II) and (I) yields an alkane and the complex (III) containing less hydrogen:



This process can be repeated. On the average every molecule may give three or four hydrogen molecules to saturate the monomer. This agrees with experimental results obtained by other workers [16].

Bashilov [17] made a detailed study of the hydropolymerisation of C_5-C_6 fractions in the presence of aluminosilicate catalysts. He showed experimentally that raising to 225–250°C the temperature of conversion of pentenes intensifies hydropolymerisation, and further rise in temperature strengthens cracking processes. The rate of redistribution of hydrogen atoms and of hydrogenation of the final reaction products is approximately the same with C_5 and C_6 alkenes.

The experimental results cited indicate the general theoretical importance of the hydro-dehydropolymerisation of alkenes on acid catalysts studied by Nametkin and his coworkers. The polymerisation of alkenes on such catalysts takes place by a cationic mechanism, in which the rate constant of chain growth is in practice usually incomparably smaller than that of termination or transfer. This extremely important fact has hitherto made it impossible to obtain products of high molecular weight by this mechanism. The cationic polymerisation of alkenes is therefore of practical interest for obtaining lower polymers, from dimers to oligomers having molecular masses of the order of a few hundreds or thousands. These oligomers are important in various branches of the chemical and petrochemical industries—the production of polymers, gasolines, lubricating oils and additives for them, the raw material for synthetic detergents, etc.—so that study of the general features and the peculiarities of the polymerisation of alkenes having various structures is not only of scientific but also of great practical interest. This governs the attention paid by research workers to the polymerisation of alkenes and several of their derivatives under the influence of various acidic catalysts. Despite the numerous papers that have appeared, many "blank spaces" still remain in our ideas on the mechanism of cationic polymerisation. However, the pioneering investigations of Lebedev and Nametkin have not lost their scientific significance even at the present time.

Experimental results confirming the hydro-dehydropolymerisation effect in several catalytic reactions of unsaturated hydrocarbons have been published even during recent years. Thus comparatively recently a study has been reported on the transformation of alkenes, cyclopropenes, alkadienes, and acetylene in the presence of $MoO_3 + Al_2O_3$. [18] The author pointed out the self-hydrogenation effects of accompanying processes of oligomerisation and isomerisation. He established that appreciable quantities of more saturated compounds than the initial hydrocarbon are formed: thus alkenes and cyclopropenes yield alkanes. The considerable quantity of hydrogen formed and of hydrogenation products found among the reaction products is regarded as indicating that the initial hydrocarbons undergo dehydrogenation on the catalyst surface followed by hydrogenation of the resulting unsaturated polymerisation products.

The experimental results are satisfactorily explained by the suggested scheme comprising—1. Dissociative adsorption of propene

$$C_3H_6\ (gas) \rightarrow C_3H_6\ (ads)\ .$$

2. Hydrogenation of propene

$$C_3H_6(ads) \xrightarrow{+H(ads)} C_3H_7(ads) \xrightarrow{+H(ads)} C_3H_8\ (gas)\ .$$

3. Dehydrogenation of propane (transfer of hydrogen to the gas phase)

$$C_3H_7\ (ads) + H(ads) \rightarrow C_3H_6\ (ads) + H_2(gas);\ 2H(ads) \rightarrow H_2\ (gas)\ .$$

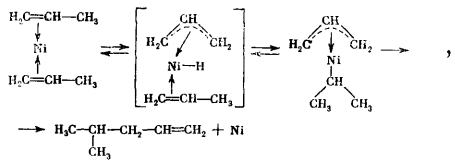
4. Formation of C_4 hydrocarbons

$$\begin{array}{c} C_3H_6(ads) + CH_3\ (ads) \rightarrow C_4H_9(ads) \xrightarrow{+H(ads)} C_4H_{10}\ (gas) \\ +H\ (ads)\ \uparrow\downarrow -H\ (ads) \qquad -H\ (ads)\ \downarrow\uparrow +H\ (ads) \\ C_3H_5(ads) + CH_3(ads) \rightarrow C_4H_8\ (ads) \rightarrow C_4H_8\ (gas) \end{array}\ .$$

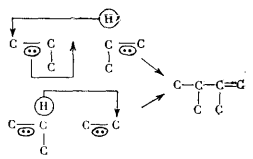
The second reaction leads to the formation of alkanes from alkenes. This may be followed by more complicated changes, in particular skeletal isomerisation. Results reported in Ref. 21 confirm and extend earlier data on the self-hydrogenation of alkenes observed in their disproportionation on $MoO_3 + Al_2O_3$ catalysts, as a consequence of which propene yields not only butene but also propane and highly unsaturated compounds.

IV. OLIGOMERISATION OF ALKENES ON TRANSITION-METAL COMPOUNDS

In all countries research workers are showing interest in the oligomerisation of alkenes on new types of catalytic systems based on compounds of transition metals. Several suggestions have been made of a reaction mechanism consisting essentially in the intramolecular transport of a hydrogen atom, i.e. with a kind of redistribution of hydrogen within the molecule. Thus in the dimerisation of propene on a complex nickel catalyst [19] the hydrocarbon undergoes oxidative addition to nickel with migration of allylic hydrogen from one propene molecule to another via an intermediate complex:



where Ni represents a coordinatively unsaturated nickel complex. Formation of a carbon–carbon σ-bond between the two coordinated alkene molecules results from activation of a carbon–hydrogen bond followed by dimerisation [18,20]:

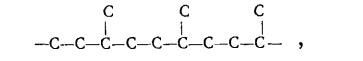


Thus the redistribution of hydrogen atoms in polymerisation processes involving alkenes on acidic catalysts, discovered by Nametkin and his coworkers, is a common phenomenon in numerous examples of the catalytic oligomerisation and polymerisation of alkenes.

V. MONOMER-ISOMERISATION POLYMERISATION ON COMPLEX ORGANOMETALLIC CATALYSTS

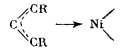
The discovery and the use of complex organometallic catalytic systems containing aluminium alkyls and their halogenated derivatives helped to establish fundamentally new routes to the synthesis of macromolecules of definite structure. This line of advance was reflected also in the study of the ionic–coordination polymerisation of alkenes catalysed by alkylaluminium halides. The application of these catalysts revealed new types of transformation, among which we shall discuss monomer-isomerisation polymerisation. The essence of this process is that isomerisation of the alkene precedes monomer addition. On the one hand this permits the polymerisation of alkenes having an internal double bond, previously regarded as unreactive. On the other hand, the possibility arises of undesirable isomerisation processes in the polymerisation of α-alkenes.

One of the first studies was made by Topchiev et al.[22] on the polymerisation of isobutene in the presence of a Ziegler type of catalyst. They discovered that the resulting polyisobutene contained fragments having the unusual structure



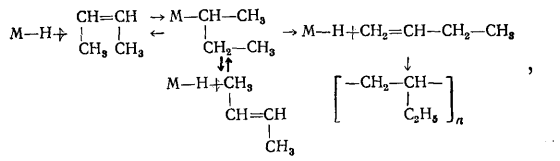
which was confirmed by numerous infrared data and also by the viscosity properties of the polymers. The occurrence of isomerisation polymerisation was suggested, but this contradicted generally accepted views on the reactivity of various cations in polymerisation processes. Unfortunately, more detailed investigations on these lines were not made, and the unusual polymerisation accompanied by formation of a polyisobutene of abnormal structure remains a matter of controversy. However, study of the polydispersity of the product by a transient sedimentation equilibrium method also showed that the structure of the polyisobutene synthesised with titanium tetrachloride plus triethylaluminium as catalyst differed from the usual polymer in a smaller degree of branching[23]. Although the polymerisation of isobutene to give the above structure is so extraordinary and improbable, the Reviewer feels that the problem is worthy of attention.

Monomer-isomerisation polymerisation[24] has been and continues to be the subject of many studies. Japanese and French workers have shown[25–32] that in many cases poly-α-alkenes can be obtained by the ionic polymerisation of β-alkenes in the presence of complex organometallic catalysts. But-2-ene was among the first β-alkenes on which monomer-isomerisation polymerisation was studied, in the presence of several catalytic systems [of which the most active comprised triethylaluminium and nickel(II) chloride] in a polar solvent, in particular pyridine. The reaction converted but-2-ene into polybut-1-ene, which was explained by isomerisation of the alkene via intermediate formation of a complex with the transition-metal compound[30–32]:



The isomerisation of alkenes having internal bonds on catalytic systems comprising an aluminium alkyl and a transition-metal compound was shown independently in experiments on several β-deuterated homologues of ethylene[33–35]. The results were interpreted on the hypothesis that two types of active centres appeared on the surface of the catalytic complex: some centres effected isomerisation of the β-alkene into an α-alkene, and the already isomerised alkene underwent polymerisation on other centres.

A reaction scheme was suggested for β-butenes as example:



where M = Al, Ni. It must be noted that isomerisation is not observed with branched alkenes.

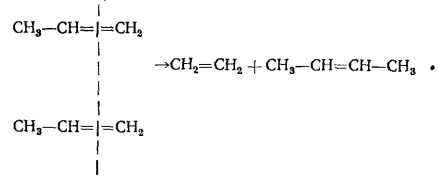
In spite of the large number of published investigations, the primary steps in a polymerisation process of this kind are still far from clear, and further detailed research is required to establish the true mechanism.

The discovery of the monomer-isomerisation polymerisation of but-2-ene is not only of theoretical interest but also of substantial practical value, since it expands considerably the raw-material base for the production of polybutene, a polyalkene possessing a valuable combination of technical properties, in particular an almost complete absence of creep.

Successful results were obtained in an investigation of the monomer-isomerisation polymerisation of pent-2-ene and hex-2-ene.[36] The plausibility of the above assumption that catalytic systems effecting monomer-isomerisation polymerisation contain two types of active centres is demonstrated by the effect of special isomerising additives on catalysts that cannot effect the process under usual conditions. Thus the monomer-isomerisation polymerisation of several higher β-alkenes can be accomplished by the use of complex organometallic catalytic systems containing acetylacetonates of certain transition metals as isomerising additives[37].

Especially noteworthy is the apparently extremely hypothetical possibility of effecting a peculiar type of isomerisation polymerisation of propene to yield from this monomer a copolymer with ethylene or (in the limiting case) polyethylene itself. Such a reaction was reported at one time by some Japanese workers in a brief communication[38], but was not subsequently confirmed.

Analogous reactions have been described in the patent literature. During recent years the disproportionation of alkenes on various types of catalytic systems has been widely used. It may be assumed that, in particular on molybdenum compounds[39,40], the disproportionation of propene yields ethylene and but-2-ene:



This may be followed by monomer-isomerisation copolymerisation of these unsaturated hydrocarbons with formation of a copolymer containing ethylene and propene units. Such a hypothesis, which has already been put forward by the Reviewer[24], undoubtedly requires experimental confirmation, especially as certain publications[41,42] quite convincingly relate the disproportionation of β-alkenes with both their homopolymerisation and their copolymerisation with other alkenes. Further research on these lines should reveal the mechanism and the characteristics of such processes.

Kennedy and his coworkers made a detailed investigation of various aspects of the cationic polymerisation and copolymerisation of alkenes, in particular of isobutene and isoprene, by means of aluminium chloride; the results have been partly summarised comparatively recently[43]. Several studies have shown[44-46] that the cationic polymerisation of isobutene and other alkenes can be accomplished by means of ethylaluminium dichloride and a hydrohalic acid. An ionic mechanism is assumed for the action of this catalyst:

$$AlR_2X + HX \rightleftarrows H^+AlR_2X_2^- \quad .$$

The resulting compound attacks the monomer:

$$H^+AlR_2X_2^- + -C{=}C- \rightarrow H-C-C^+AlR_2X_2^- \quad .$$

This is followed by the actual polymerisation:

$$H-C-C^+ + C{=}C \rightarrow H-C-C-C-C^+ \rightarrow \text{Polymer} \quad .$$

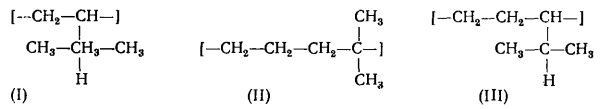
It must be noted that bimolecular protonation of the monomer is accompanied by unimolecular protonation of the gegenion. This results in formation of the saturated hydrocarbon and the corresponding aluminium dihalide:

$$H^+AlR_2X_2^- \rightarrow HR + AlRX_2 \quad .$$

Kennedy gave[43] several experimental results on the role of such factors as the nature of the solvent in the cationic polymerisation of alkenes by means of catalytic systems based on aluminium alkyls. As was to be expected, the solvent had a significant influence both on the kinetics of polymerisation and in many cases on the structure of the polymer chain.

Saegusa et al.[47,48] made a series of interesting investigations on the cationic polymerisation of several alkenes by means of systems containing aqueous triethylalumium alone and with methoxymethyl chloride. The polymerisation was studied[49] not only of well known hydrocarbons but also of the little studied 2-methylpenta-1,3-diene, 1-isopropylindene, and 3a,4,7,7a-tetrahydroindene using catalysts of a similar type, and also paid attention to isomerisation.

Recent work by Kennedy et al.[50] has demonstrated the monomer-isomerisation polymerisation of 4-methylpent-1-ene on ethylaluminium dichloride in chloroethane at −30 to −90°C. The presence of at least the three isomeric units

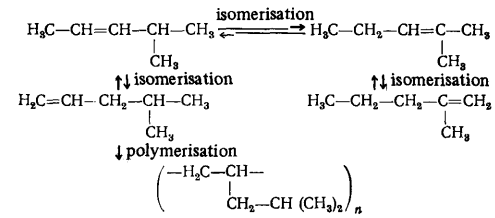


(I) (II) (III)

in the products was detected by ^1H n.m.r. (with a resolution of 300 MHz).

Still later publications[51,52] reported the monomer-isomerisation polymerisation (by means of catalysts of the Ziegler–Natta type) of several branched alkenes, in particular 4-methylpent-2-ene and 4-phenylbut-2-ene, as well as the copolymerisation of linear β-alkenes, of but-2-ene with pent-2-ene and of hex-2-ene. The maximum yield of the copolymer—a poly-α-alkene—reaches ~18% in the presence of triethylaluminium with vanadium or titanium trichloride as catalytic system at 80°C. The content of isomerised units in the polymer increased when the catalytic system contained nickel dimethylglyoxime or an acetylacetonate of another transition metal.

Subsequent studies by Japanese workers[53] have shown that the monomer-isomerisation polymerisation of 4-methylpent-2-ene catalysed by triethylaluminium with titanium trichloride gives a high yield of a macromolecular isotactic 4-methylpent-1-ene component. As in the preceding case, the presence in the reaction medium of acetylacetonates of transition metals, e.g. nickel acetylacetonate, increases the rate of isomerisation of the monomer. The monomer-isomerisation polymerisation of 4-methylpent-2-ene can be represented by the scheme



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The Reviewer has thus attempted to show (only on two examples) that a detailed study of the polymerisation of alkenes led to the discovery of unexpected effects, forcing a re-examination of existing views on the reaction mechanism. One such effect was discovered at the beginning of research on polymerisation as a branch of organic chemistry, and another has attracted attention during recent years in connection with the discovery of new catalytic systems and the establishment of macromolecular chemistry as an independent field of chemical science.

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