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Consequences and development of an invention*

Nobel Lecture, December 12, 1963

The awarding of the Nobel Prize for Chemistry for the year 1963 is related to the precipitous expansion of macromolecular chemistry and its industrial applications, which began precisely ten years ago at my Max-Planck-Institute for Coal Research, in Mülheim/Ruhr. The suddenness with which this began, and the rapidity with which it was propagated are comparable to an explosion. The energy carriers in this case were the ingenuity, activity, creative imagination and bold concepts of the many unnamed chemists, designers and entrepreneurs in the world who have fashioned great industries from our humble beginnings.

If today I stand with my colleague Natta, who has been particularly effective in promoting this explosive wave, in the limelight of distinction, and do wish to manifest, with this address, my appreciation for the honor bestowed upon me, I must begin by thanking these many anonymous persons. They, too, deserve this distinction.

The extent of this "explosion" may be illustrated by two charts¹, in which the location of newly-established plants is indicated. The places marked by black circles refer to the production of high molecular weight materials, the crosses to new production facilities which, though concerned with low molecular weight materials, nevertheless also have some connection with the address I am delivering today (Figs. 1 and 2).

The new development had its inception near the end of 1953, when I, together with Holzkamp, Breil and Martina, observed-during only a few days of an almost dramatic course of events-that ethylene gas will polymerize very rapidly with certain catalysts that are extremely easy to prepare, at 100, 20 and 5 atmospheres and, finally, even at normal pressure, to a high molecular weight plastic.

I would like to first describe our normal-pressure polymerization experiment, which actually takes about an hour but which has been condensed in the films to a few minutes (not shown here).

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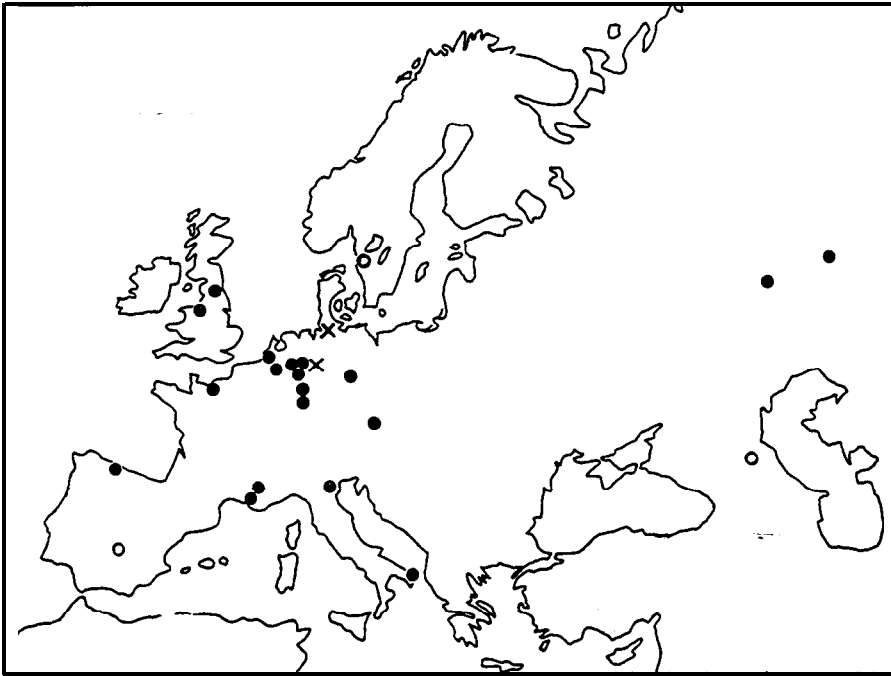


Fig. 1. Location of industrial applications of the Mülheim processes in Europe (as of 1963). On the figure: ● High molecular weight materials; x , Aluminium alkyls and low molecular weight materials; c, Under construction or planned.

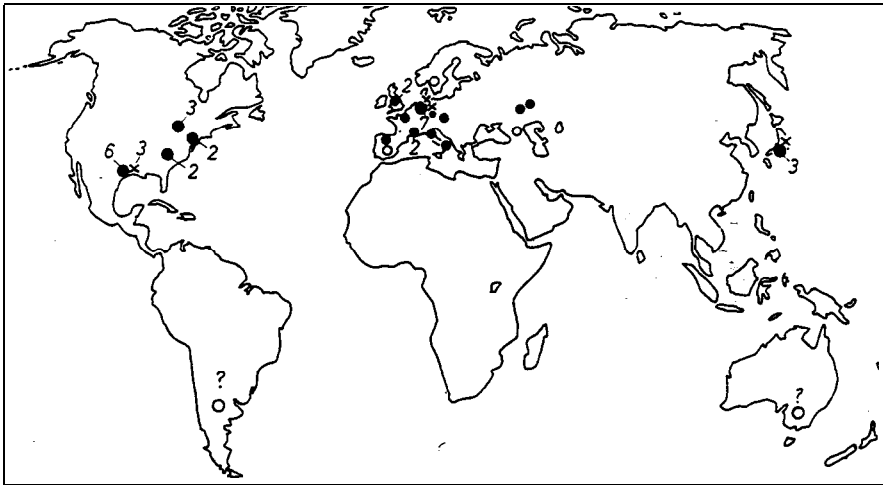


Fig. 2. Location of industrial applications of the Mülheim processes in the world (as of 1963). Symbols as in Fig. 1. Numbers indicate the number of factories.

The catalyst is prepared simply by simultaneously pouring, with exclusion of air, two liquid materials into about two liters of a gasoline-like hydrocarbon, after which ethylene is introduced, while stirring. The gas is absorbed quickly; within an hour one can easily introduce 300-400 liters of ethylene into the two liters of liquid. At the same time, a solid substance precipitates, in such a way that after approximately one hour the material becomes doughy and can scarcely be stirred any more. If the brown catalyst is then destroyed, by the addition of some alcohol and by the introduction of air, the precipitate becomes snow-white and can be filtered off. In its final state it will accumulate, in amounts of 300-500g, as a dry, white powder.

The results of this experiment greatly surprised us, and, later on, many others, since up to that time ethylene had been considered extremely difficult to polymerize. The "polythene" of the Imperial Chemical Industries, a product which had been known for some seventeen years, was being prepared under pressures of 1000-2000 atmospheres, and at a temperature of 200°C. Our experiment thus destroyed a dogma. It led, in addition, to a polyethylene which differed quite markedly from the high-pressure product. Low-pressure polyethylene not only has a better resistance to elevated temperatures and a higher density, but is also more rigid. This is easily demonstrated by holding in one hand two similar objects made of the two materials, and press-

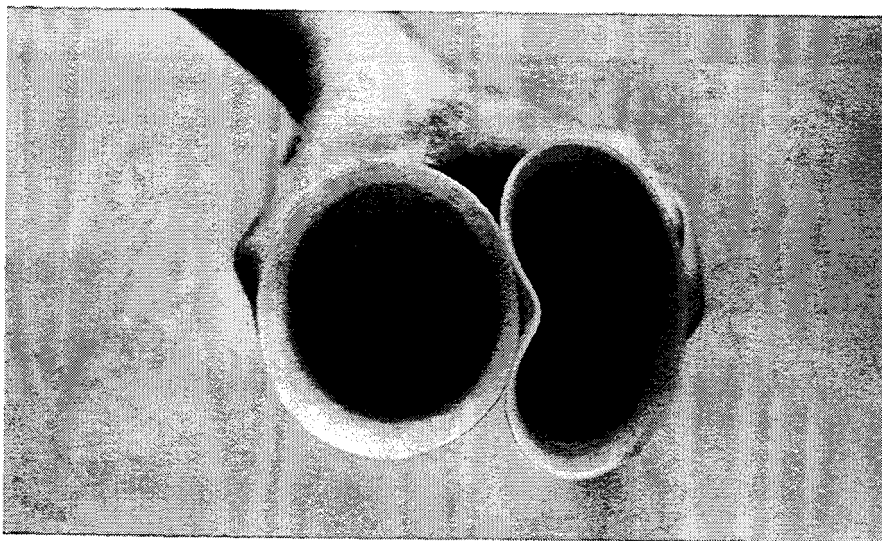


Fig. 3. Comparison between the rigidity of two beakers, one of low-pressure, one of high-pressure polyethylene.

ing them together (Fig. 3). Low-pressure polyethylene can be drawn without difficulty to form fibers or ribbons of high tensile strength. This cannot be done at all with high-pressure polyethylene, or at best only an indication of drawing is obtained. We established these facts immediately after our discovery, with test specimens which were still quite primitive¹.

The differences can be attributed to the fact that in our process molecules of ethylene are joined together linearly, without interruption, whereas in the high-pressure process chain growth is disturbed, so that a strongly branched molecule results (Fig. 4).



Fig. 4. High-pressure polyethylene, structural principle.

The low-pressure process found immediate acceptance in industry. By 1955, 200 metric tons of this new type of plastic had been produced; in 1958 it was 17000 tons, and in 1962 some 120000 tons. The much higher figures occasionally cited for this and other plastics have resulted from the confusion of available, but unused, capacities with actual production. The increase in dimensions can be indicated by comparison of our first test specimens, prepared ten years ago with rather primitive means, with containers that are twenty cubic meters in capacity, the largest now being made from polyethylene. A subsequent figure shows the lightness of the material, since a very large container can easily be carried by only a few men.

The catalyst employed in the experiment described was prepared by mixing aluminium triethyl, or diethyl aluminium chloride, with titanium tetrachloride. However, this is only one example, taken from the countless series of "organometallic mixed catalysts". Most generally they will form, as we found, whenever standard organometallic compounds, preferably those of aluminium, but also many of other metals, are brought into contact with compounds of certain heavy metals. Those of titanium, zirconium, vanadium, chromium, molybdenum, cobalt and the like are especially effective. Since

there are many different metal alkyls and many different heavy metal compounds, and since, furthermore, components can be mixed together in varying proportions, and by different methods, and because all this can have an effect, often a truly decisive effect, on the nature of the catalytic activity, it is easy to understand why this field has grown to practically limitless proportions.

In place of the metal alkyls, one can also use metal hydrides, or the metals themselves, whereas metal alkyls probably will still form during the catalyzed processes.

Our catalysts then became known, at the turn of the year 1953/4, to our friends in industry and to their foreign colleagues, in Frankfurt, the Ruhr, Manchester, and-last but not least-Milan. Shortly thereafter this knowledge jumped over to the U. S. A. as well, and ultimately our findings became available to all. The consequences have been characterized, elsewhere, by the statement that revelation of the Mülheim catalysts had the same effect as the starting gun of a race in which the laboratories of the interested industries had been entered⁴. However, representatives of purely scientific chemistry also participated.

Because of the magnitude of the new field, arrival at further stages, or the order of such arrivals, was necessarily dependent upon contingencies. Indeed, many important observations were made within short spaces of time, independently of one another, and at different places. Let me illustrate this with two examples: It was pure chance that in November of 1953 the first of the catalysts in which our invention was clearly recognizable happened to be a relatively weak-acting combination of an aluminium alkyl with a zirconium compound, by which ethylene could be polymerized only under a few atmospheres pressure, and with which propylene, already tested the day after our critical experiment with ethylene, would not polymerize at all. Then, for a number of weeks, we were absorbed in experimenting with normal-pressure polymerizations of ethylene by means of titanium-containing catalysts. Early in 1954 we recognized the possibility of copolymerizing ethylene and propylene, after which we succeeded, at Mülheim, in polymerizing propylene with more effective catalysts, but - and this we did not know at the time - a short while after my colleague Natta of Milan had already observed this. In a first substantiation of his observation, and in an act of fairness, Natta had referred to the catalyst used as a "Ziegler catalyst", and that is how this expression found its way into the literature⁵. It is surely understandable that I myself prefer to speak of them as "Mülheim catalysts".

The second example: Near the close of 1955 work was being done in many

places on the polymerization of butadiene with our catalysts. But no one had observed that in addition to the desired high polymers, a very interesting trimer of butadiene, namely 1,5,9-cyclododecatriene, was being produced. Günther Wilke, of my institute, became aware of this, and showed how one can guide the reaction entirely in this new direction. While endeavouring to explain the formation mechanism of cyclododecatriene, Wilke discovered a way to redirect this reaction at will, either toward a dimerization to an eight-membered ring, or - by a co-reaction with ethylene - toward a co-oligomerization to a ten-membered ring⁶. The result was that the Mülheim catalysts also achieved importance for polycondensation plastics such as Nylons 8, 10 and 12, into which the ring compounds can be transformed.

These cyclizations constituted the third surprising development afforded the scientific community by the organometallic mixed catalysts, if I assign number one to the new polyethylene process. I saved the second surprise for

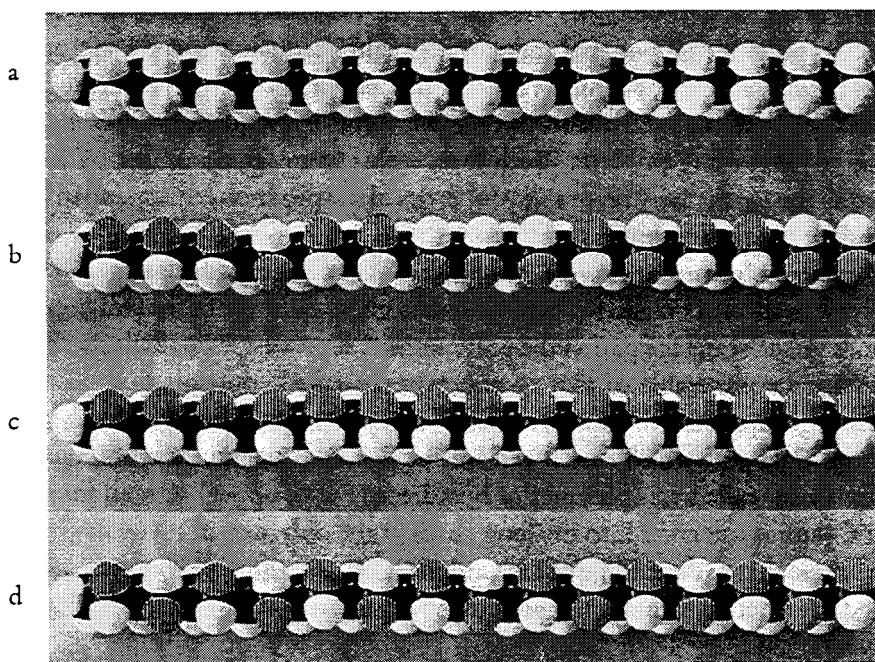


Fig. 5. Portions of the chains of (a) polyethylene, (b) atactic, (c) isotactic and (d) syndiotactic polypropylene. The methyls in the polypropylene are striped, and are actually much larger than shown.

later, and I must go into that now. From the middle of 1954 on, it began to be obvious that the Mülheim catalysts were capable of polymerizing in a structurally specific, as well as a stereo-specific manner. This realization is an essential contribution of my colleague Natta. He had often pondered over the mechanism of the polymerization, and very successfully strove to "train" the catalysts in such a way that they would possess extremely high specificity. Without wishing to anticipate Natta⁷ in any way, I nevertheless feel obliged, for the sake of completeness, to explain briefly what this is all about.

The chain of linear polyethylene in the model, at an enlargement of fifty million, has approximately the following shape: (Fig. 5a). If a substituted ethylene, for example propylene, is polymerized, only the two doubly-bound carbon atoms of the olefin molecule will participate in the chain formation. The substituents, *as* side chains, will remain on the outside. If they combine in a purely random fashion the resultant product will show an entirely arbitrary distribution of the substituents along the two sides. Previously it had been believed that only those polymers could be formed which Natta - so far as I know at the suggestion of his wife - later called "atactic" (Fig. 5b). In stereo-specific polymerizations, polymers with highly regular structure are produced, with all the substituents on one side - isotactic (Fig. 5c) according to Natta - or with the substituents in a regular right-left sequence - syndiotactic (Fig. 5d) according to Natta. Both these terms were again inspired by Mrs. Natta. The particularly favorable properties of the products correspond to the regularity of the structure.

Analogous phenomena were encountered when our catalysts were used for polymerization of butadiene. In this instance, either only one of the two double bonds present can take part in the polymerization process. The result is a configuration comparable to that of polypropylene and containing, instead of methyl groups, only the unsaturated residues of ethylene, the so-called vinyl groups C_2H_3 , in which case it can still be isotactic, atactic, or syndiotactic. This is a so-called 1,2-polymer of butadiene (Fig. 6, upper). Or, all four of the C-atoms can enter into the long chain of the polymer, in 1,4-polymerizations, so that in the middle of each individual C_4 structure unit a new double bond is formed, which was not present previously at that particular site (Fig. 6, lower).

In addition, because of the double bonds, and from their aspect, the valences of the two adjacent carbon atoms point either both toward one side, or to opposite sides. The first is the *cis* configuration, and the other is the *trans* (F i g . 7) .

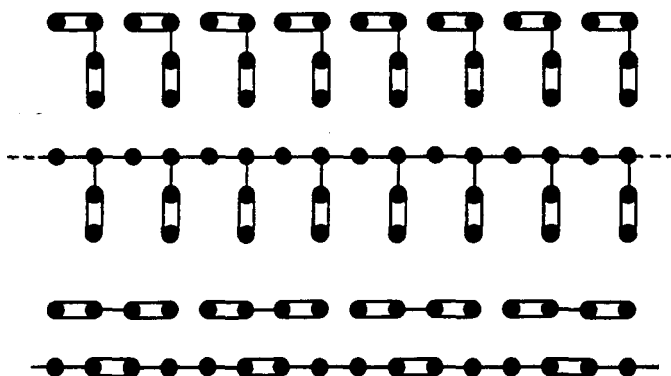


Fig.6. "1,2-"(upper) and "1,4-"(lower) polymerizations of butadiene. Hydrogenatoms are not shown.

Natural rubber is a *cis*-1,4-polybutadiene, in which, are very disable bond, the hydrogen atom has been replaced by a methyl group. Another important natural substance, guttapercha, corresponds to the *trans*-1,4-polymer(Fig. 7). The difficulty with all earlier attempts to synthesize rubber or rubberlike materials was that it was not possible to steer the polymerization of the basic materials - butadiene, isoprene - uniformly into the one or the other configuration. For this reason synthetic products contained a chaotic array of 1,4-*cis*, 1,4-*trans* and 1,2 structural units, even in the individual molecules. Although they resembled the natural product to some extent, none of them ever corresponded to it completely.

With the aid of the easily prepared Mülheim catalysts it is now possible to synthesize all these types uniformly, as desired, in a structure-specific or stereospecific manner. For example, 1,2-polybutadiene is formed by using a

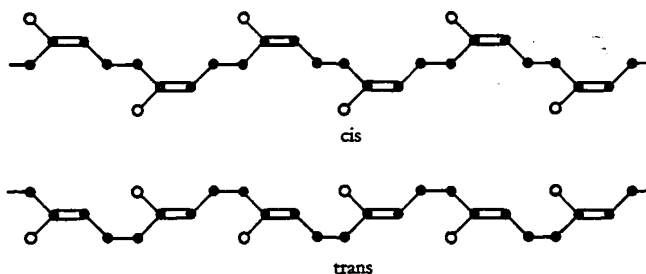


Fig. 7. Structural principle of natural rubber (*cis*) and guttapercha (*trans*). White circles: methyl groups. Hydrogen atoms are not shown.

catalyst made from titanium acid ester and 3 aluminium triethyl. With the catalysts obtained from $\text{TiCl}_4 + 0.5 \text{ Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, *trans*-1,4-polybutadiene can be produced, and with those derived from $1 \text{ TiI}_4 + 1 \text{ Al}(\text{C}_2\text{H}_5)_3$ or $1 \text{ CoCl}_2 + 1 \text{ Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, *cis*-1,4-polybutadiene will be formed. Finally, I would like to add that an increase of the Al : Ti ratio in the catalyst, to 5 : 1, will lead to cyclododecatriene.

A group from the B. F. Goodrich Research Center in the U. S. A. first made these observations with *cis*-1,4-polyisoprene, the synthetic "natural rubber", a few weeks; after their company had learned about the essential features of our catalysts⁸. Actually, this represented only the final, closing stages of a 50-year effort to synthesize "genuine" rubber. Corresponding polymers of butadiene itself were then intensely studied, in a number of places, and *cis*-1,4-polybutadiene is today considered to be of great technological importance.

I will close this short survey with a discussion of recent developments pertaining to the rubber-like copolymers of ethylene and propylene, particularly those obtained with vanadium-containing organometallic mixed catalysts, and to the so-called terpolymers, into whose molecules certain diolefins - (dicyclopentadiene, or, again as discovered by Natta and coworkers⁹, our cyclooctadiene-1,5) - have been incorporated.

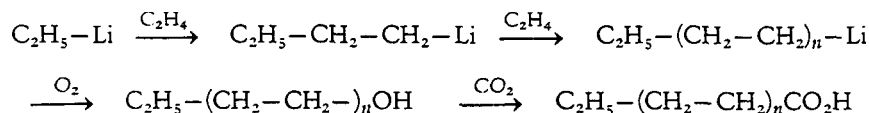
Large quantities of all these new synthetic materials, discovered in connection with low-pressure polyethylene, are already being produced throughout the world, and production is sure to continue rising at a substantial rate.

With this I have shown, in broad outline, what has resulted in the course of ten years from our early experiments with organometallic mixed catalysts. In order to make the sequence of events which led to such a fruitful invention more understandable, I shall have to go back exactly forty years. Shortly after my graduation, having been a student of Karl von Auwers at the University of Marburg/Lahn, I began my independent scientific work with experiments for testing the theory of so-called free radicals. I incidentally found, in 1923, a new method for the formation of organic compounds of the alkali metals potassium and sodium¹⁰, which brought my attention to the metal alkyls as an interesting, highly diversified field, that has continued to fascinate me, over and over again, up to the present. The new catalysts grew out of this, as a side sprout, in 1953. Permit me now to pursue the unbroken chain of causal relationships that links Then and Now by using special block schemes (Fig. 8, 0 → 1, Figs. 9-12).

A few years later, in 1927, Bähr and I¹¹⁻¹³ made the discovery - important

With Colonius¹⁴, I was able to confirm this in 1930, and that is how the organolithium compounds became easily accessible (Fig. 8,3).

In Mülheim/Ruhr, where I have been working since 1943, Gellert and I succeeded in transferring the technique of a "stepwise organometallic synthesis" from butadiene to ethylene¹⁵. In this instance the reaction leads from lithium alkyl directly to the higher straight-chain lithium alkyls, and hence also to alcohols, carboxylic acids, and the like (Fig. 8,5).



Contrary to what holds true for butadiene, however, there is a limit here to the growth which a chain can undergo, since, for ethylene addition, the temperatures required are such that the lithium alkyls will readily decompose to lithium hydride + olefin. This certainly seemed to justify the following conclusion: If, in such decompositions, it is a question of a reversible reaction, as we had reason to believe, then lithium hydride and lithium alkyls should, under proper conditions, function as catalysts for the polymerization, or rather, oligomerization, of ethylene to the higher α -olefins (Fig. 8, 6).

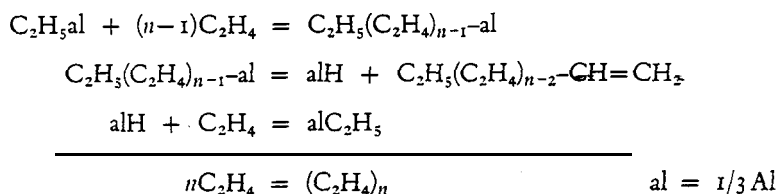
We did find such a reaction in principle, but it was so complicated by secondary and subsequent reactions that we could do nothing with it. Then when I had already decided to give up these efforts, my coworker, H. G. Gellert, conducted one more experiment-and the last, he was convinced-with the just recently discovered lithium aluminium hydride. This led immediately to the desired higher α -olefins (Fig. 8, 7). As the decisive turning point, this resulted in the realization that the alkali metal was not the crucial issue at all, and that everything we already knew about the lithium alkyls, and all that we had anticipated besides, with respect to the chemistry of the olefinic hydrocarbons, could be achieved with a great deal more ease through use of organoaluminium compounds¹⁶. That is:

- (1) There are genuine equilibria aluminium alkyl + aluminium hydride + olefin lying, as a rule, entirely to the left, so that, in reverse of the situation with lithium, it is possible to synthesize the aluminium alkyls from hydride + olefin (Fig. 8, 8,9).
- (2) In the case of aluminium, too - and this came as a real surprise - at moderately high temperatures a stepwise organometallic synthesis, or as we now

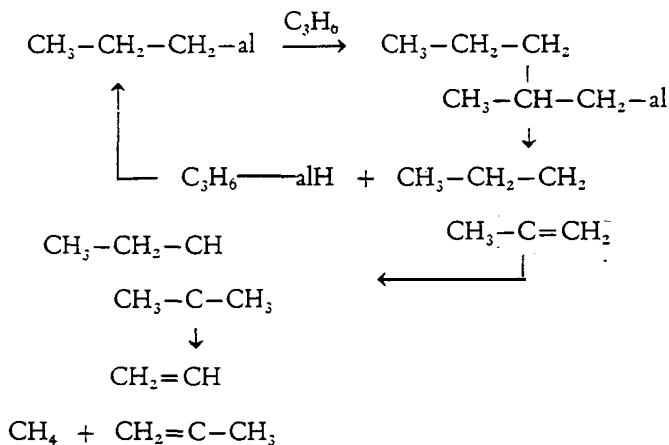
call it, a "growth" or propagation reaction takes place, leading to the higher aluminium alkyls; thus, a synthesis of the higher straight-chain primary monofunctional aliphatic compounds, particularly the fatty alcohols (Fig. 9, 10,11), became possible.

(3) Furthermore, we have, from about 150° on, a catalytic oligomerization of the ethylene to higher α - olefins (Fig. 9, 21).

Here the organometallic synthesis appears as the partial reaction of a completely understood, homogeneous intermediate reaction catalysis: After a certain number of addition steps the intermediate product decomposes to a hydride and an olefin whereupon, after the addition of ethylene to the hydride, the cycle is repeated.



Such a reaction was encountered in its most primitive form with propylene, for which the homogeneous catalysis leads, without supplementary chain growth, almost exclusively to a well-defined dimer¹⁷ (Fig.9, 19):



Recently this reaction has achieved significance for high molecular weight chemistry as well, since the cracking of isohexene, following the shifting of the double bond, produces isoprene, in addition to methane¹⁸ (Fig.9, 20).

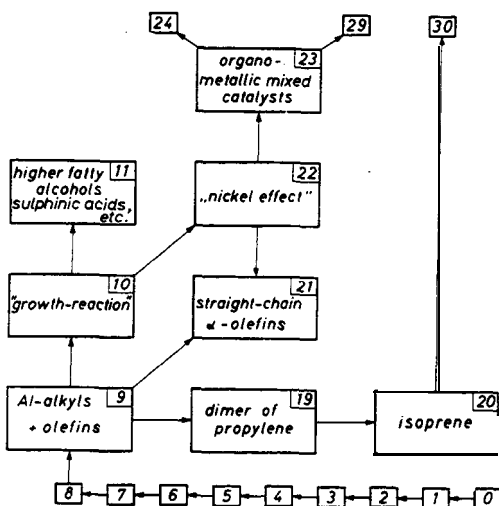
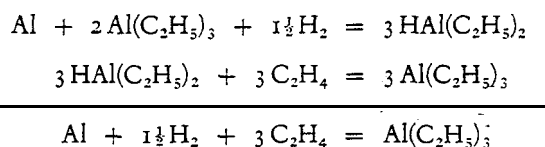


Fig. 9. Course of the Mülheim Experiments, Part I.

The transition of all these reactions into industrial applications was finally accomplished by the so-called "direct synthesis" of aluminium alkyls from aluminium, hydrogen and olefins, discovered by us at approximately the same time as the new polyethylene process. Aluminium hydride, from which the aluminium trialkyls are quite easy to obtain through the addition of olefins, cannot be prepared directly from the metal and hydrogen. However, in already-prepared aluminium trialkyls, aluminium will dissociate with hydrogen to dialkyl aluminium hydrides which, with ethylene, will give 1.5 times the original amount of aluminium triethyl,



so that any amount of aluminium trialkyl can be prepared without difficulty¹⁹ (Fig.10, 12,14).

In the charts shown at the beginning of this address, the location of the industries engaged in the production of aluminium alkyls and their low molecular weight applications were included. This area of the industrial development initiated by Mülheim is likewise in a state of continuous evolution, though it has been less rapid than that of the high molecular weight phase.

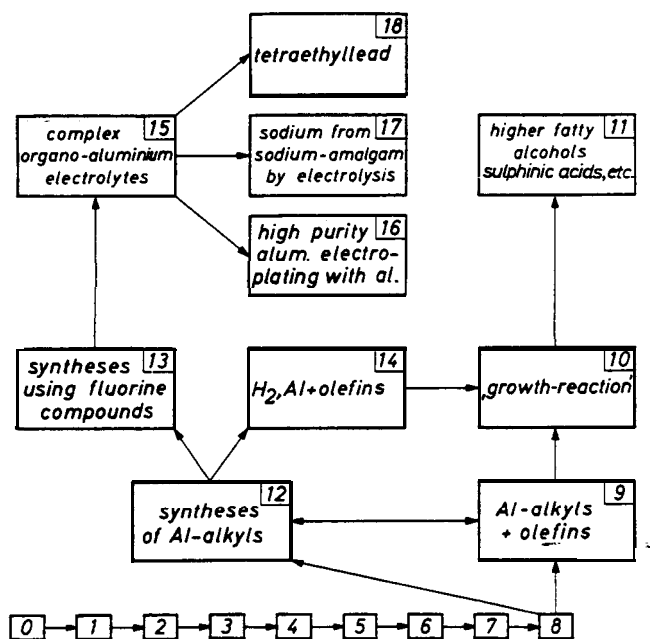
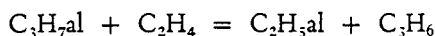


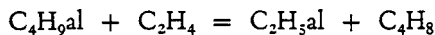
Fig. 10. Course of the Mülheim Experiments, Part II.

Up to the year 1952 we had frequently conducted "growth" reactions based on aluminium triethyl, and thought we were thoroughly acquainted with such reactions. But when, together with E. Holzkamp²⁰, I attempted to apply this type of reaction to aluminium tripropyl the formation of chains, to our great surprise, did not materialize at all. On the contrary, we obtained propylene-from the propyl aluminium - in addition to aluminium triethyl and α -butylene. Even starting from aluminium triethyl our reaction now yielded nothing but butylene and the unchanged aluminium compound.

The explanation was obvious: A catalyst in trace amounts must have gotten into this series of experiments, leading to an uncommonly rapid acceleration of the displacement reactions:



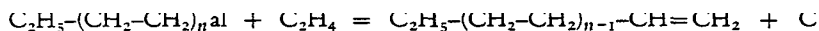
and



Under such conditions the alkyl had to be forced out at the aluminium, immediately after the first propagation step, as butylene. It is now generally

known that we detected a tiny trace of metallic nickel as the disturbing element² (Fig. 9, 22). Thus our attention was again directed to the problem to polymerize also ethylene just as, years ago, we had been able to do with butadiene and styrene, to produce a genuine macromolecule with the aid of metal alkyls, in this case aluminium alkyls in particular.

Our growth reaction must lead to a genuine polyethylene, if we succeeded in adding about 1000 ethylene units to the aluminium triethyl. For this, with our reaction, only about 100-200 atmospheres pressure, instead of the 1000-2000 atmospheres used heretofore, would be required. Nevertheless, in properly performed experiments we had obtained only waxy products, because the chain at the aluminium was prematurely split off—apparently by a displacement reaction—as an olefin, with there-formation of ethyl at the aluminium, an occurrence known to chemists working in the high molecular weight field as a "chain transfer reaction":



To the extent that catalyst traces, as we now might well suspect, had been involved here also in effecting the displacement, there existed the prospect that completely "aseptic" procedures could eventually lead to a true polyethylene. In order to provide the essentials for the "asepsis", we began, in the middle of 1953, to systematically investigate substances which have effects somewhat similar to those of nickel. We found, instead, the polymerization-promoting organometallic mixed catalysts, and, in particular, we achieved a low-pressure polymerization of ethylene, and with this I have again arrived at my starting point (Fig. 9, 23).

Fig. II, which follows, once again shows, in schematic form, all that has resulted from the discovery of organometallic mixed catalysts. In this connection, isoprene is doubly concerned in our work: because of the aforementioned synthesis, and for polymerization purposes.

Finally, I would like to present the following scheme (Fig. 12), in order to show the entire development. The areas in two types of hatching indicate the important transitions (from Li to Al, from the Al-alkyls to the mixed catalysts), and also a third transition to an electrochemical side branch, which I cannot go into at this time (cf. Fig. 10, 15 → 18). The important consequences of the discovery of organometallic mixed catalysts, evident even to the layman, have led many to regard me, nowadays, as a "macromolecular chemist", and, in fact, even as a plastics expert. I have intentionally set my work in this field within a much broader framework, to show you that I am a "macro-

molecular chemist" only peripherally, and that I am not at all a plastics expert. Rather, I have always looked upon myself as a pure chemist. Perhaps that is also why the impact of the invention has been so enduring. The new knowledge has, after all, not come from macromolecular chemistry. It is the metal alkyls that have insinuated themselves into the chemistry of macromolecules to effectively fertilize this field. Typical of the course I have followed from those early beginnings of forty years ago until today, is the fact that I have never started with anything like a formally presented problem. The whole effort developed quite spontaneously, from a beginning which was actually irrational in nature, through an unbroken causal series of observations, interpretations of findings, rechecking of the interpretations by new experiments, new observations, etc. My method resembled a meandering through a new land, during which interesting prospects kept opening up, during which one could frequently view part of the road to be traveled, but such that one never quite knew where this trip was actually leading. For decades I never had the slightest notion that successful technological and industrial applications were also to be encountered during the journey.

Twice this path seemed seriously blocked. The first time was before the transition from lithium hydride to lithium aluminium hydride and from the lithium to the aluminium compounds had been accomplished. The second was when our growth reaction suddenly, in a truly mysterious way, refused to go any more. In both cases, a capitulation in the face of these difficulties would undoubtedly have broken the red thread of continuity, which can now be followed clearly.

But a much more formidable impediment might have presented itself. In order to illustrate this, I must elaborate on the paradox that the critical concluding stages of the investigations I have reported took place in an institute for "coal research".

When I was called to the Institut für Kohlenforschung in 1943, I was disturbed by the objectives implied in its name: I was afraid I would have to switch over to the consideration of assigned problems in applied chemistry. Since ethylene was available in the Ruhr from coke manufacture, the search for a new polyethylene process, for example, could certainly have represented such a problem. Today I know for certain, however, and I suspected at the time, that any attempt to strive for a set goal at the very beginning, in Mülheim, would have completely dried up the springs of my creative activity. As a matter of fact: Giving up my preoccupation with organometallic compounds in favor of the other, "bread-and-butter" problems of coal chemis-

try - many of my colleagues were of the opinion, at the time, that this would be the natural consequence of my removal to Mülheim - would have cut the leads which I already held invisibly in my hand, and which were to lead me safely to the results that proved of such importance also for the Ruhr industry.

As a condition of my transfer to Mülheim I stipulated that I was to have complete freedom of action in the entire field of the chemistry of carbon compounds, without regard to whether any direct relation to coal research was or was not recognizable. The acquiescence of my stipulation was in accord with the principles of the then Kaiser-Wilhelm, and now Max-Planck Society, of which my institute is a part. As far as the German coal mining industry which supported my institute is concerned, this was an act of great foresight on their part which did in fact provide the conditions for everything that occurred, particularly the present circumstance that my institute, and I with it, have now received this very great distinction.

The institute, however, - what is it, in its distinctive spritual and intellectual substance, other than the totality of its active people. I began this address with an expression of gratitude to the many people in the world whom I know only slightly, or not at all, and who have developed great industries from our beginnings. I will end the address by expressing my heartfelt thanks to the many, very well known members of my institute who have stood by me faithfully throughout all these years, and who share with me the prize for which I have been singled out.

1. Figs. I-II are taken from K. Ziegler, *Arbeitsgemeinschaft. Forsch. des Landes Nordrhein - Westfalen*, 128 (1964) 33.
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