THE ZIEGLER CATALYSTS
SERENDIPITY OR SYSTEMATIC RESEARCH?

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Fifty-four years after the Nobel Prize was awarded to Karl Ziegler and Giulio Natta for the polymerization of olefins by complex organometallic catalysts, the field continues to elicit enormous interest, both from the academia and the industry. Furthermore, this chemistry and technology occupy a high ground in the annals of 20th-century science. The elegance and simplicity of Ziegler's chemistry continue to astound researchers even today, and the enormous impact this chemistry has had on the quality of our life is truly incredible. Polyethylene, produced using Ziegler's chemistry has touched every aspect of common man's life, so much so that, today it is impossible to imagine life on this planet without polyethylene. Equally fascinating is the story of how Ziegler stumbled on this most impactful discovery. Ziegler's discipline and rigor in systematically following every lead in the laboratory, however trivial it seemed, and his penchant for understanding the basics of science culminated in 1954, with a simple reaction for converting ethylene to polyethylene, the quintessential carbon-carbon (C-C) bond forming reaction. His life and work hold many lessons for all scientists who dream of making their scientific quests useful and relevant to society. It is also relevant to the contemporary debate on basic versus applied research.

KEYWORDS
Organometallic catalysts, organoaluminum, organolithium, organonickel, olefins, carbonmetal bond, Ziegler's catalysts, polyethylene, LDPE, HDPE, serendipity.

KARL ZIEGLER: LIFE AND TIMES

Karl Waldemar Ziegler was born on 26 November 1898, in the town of Helsa, near Kassel, Germany, (Figure 1). He was educated at the University of Marburg from where he obtained his PhD in 1920, working under the supervision of Professor Karl von Auwers. His thesis was titled 'Studies on Semibenzole and Related Links'. It is interesting to note that Professor von Auwers' claim to fame were two of his students, one of whom was Karl Ziegler and the other Georg Wittig!

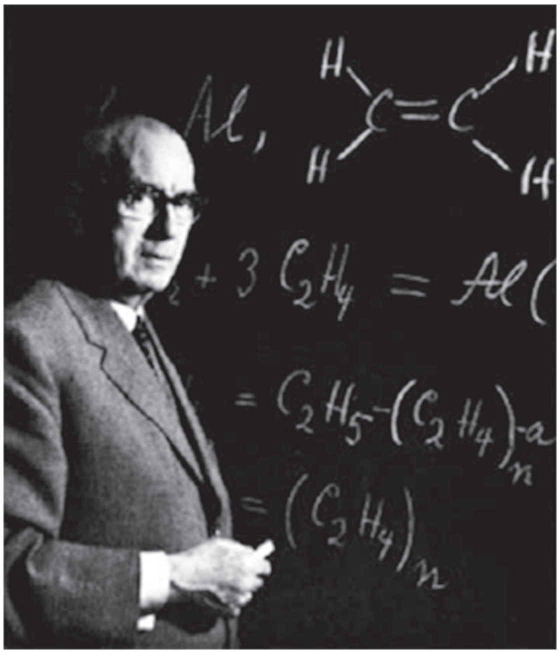

FIGURE 1: PROFESSOR KARL ZIEGLER.

Ziegler began his academic career at the University of Marburg; thereafter, he had a brief stay at the University of Frankfurt and then moved to the University of Heidelberg in 1926. In 1936, he moved to the University of Halle-Saale (now Martin Luther University Halle-Wittenberg) as a Professor and the Director of Chemical Research before finally moving to the Kaiser Wilhelm Institute for Coal Research at Mulheim an der Ruhr in 1943. When he received the invitation from the Kaiser Wilhelm Institute, Ziegler was pleasantly surprised. In Ziegler's own words, and I quote, "I must admit that my immediate reaction was completely negative. There were good reasons for this: in my scientific career, I had experienced happy years in which my work was guided purely by the pleasure of working on the problems that I had chosen myself, even though this was within the framework of the modest resources of a university professor of chemistry. Moreover, the period of directed research immediately preceding had made it clear to me that I was less suited for projects with predetermined aims. With just a few exceptions, my research had developed from observations that had been made during the immediately preceding work. I was very convinced of the fruitfulness of the policy of allowing my work to develop from the interaction of observation, theoretical interpretation, and new experiments, without regard to the fields into which this would lead me. It is therefore quite natural that I was disturbed that the name of the institute (where a position was) being offered to me expressed its purpose. I insisted that I must be given complete freedom to pursue the entire field of compounds of carbon ('organic chemistry') irrespective of whether a clear relationship could be recognized between my work and coal or not."

It was here that Ziegler conducted his path-breaking work on organoaluminum chemistry that eventually led to the discovery of the family of catalysts that bears his name – 'Ziegler's catalyst', and the discovery of a low temperature-pressure process for the preparation of linear polyethylene that transformed the world of industrial chemistry as well as polymer science and became one of the most successful innovations in the history of chemical science. In a sense, Ziegler's accomplishment is one of the greatest ironies of our time; an individual whose only aim was to pursue interesting, curiosity-driven science, became responsible for creating one of the largest industries of the 20th century. In Ziegler's own words, "I set out to follow a broad course of study in which my only guide was, initially, just the desire to do something which gave me pleasure. The course threw up many interesting conclusions, many of them of highly practical value, and one of them led ultimately to a method of making polyethylene" [1].

Karl Ziegler passed away on 11 August 1973, at Mulheim, leaving behind a rich legacy of chemistry, industry, and wealth, both to himself and to the institution he served.

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Ziegler lived and worked during some of the most turbulent times in world history. He saw Europe being torn asunder during the two World Wars, bringing in its wake enormous disruption as well as economic, political, and moral turmoil. He witnessed the emergence of National Socialism in Germany in the late 1930s, which he found to be repugnant and rejected vehemently. Given his views, he was not invited to a professor's position till 1936, almost thirteen years after his habilitation. Yet, it is a tribute to his dedication to science and the force of his personality that he came out of World War II unscathed, in terms of his political association and personal reputation.

Ziegler won the Nobel Prize in Chemistry in 1963, which he shared with G Natta. The citation read, for their discovery in the field of chemistry and technology of high polymers. The title of his Nobel lecture was 'Consequences and Developments of an Invention.' There are two essential observations concerning this Nobel worth making a note of. One, between 1912 (Victor Grignard) and 2005 (Grubbs, Shrock, and Chauvin) as many as ten Nobel, Prizes have recognized scientists who have demonstrated new ways of making C-C bonds – a quintessential reaction in chemistry. Second, by the time Ziegler and Natta walked the aisle in Stockholm, industrial manufacture of polyethylene and polypropylene had commenced, and they were commercial products in the market. I am not aware of any other claimant to the Nobel who can speak of such an achievement!

ZIEGLER'S CONTRIBUTIONS TO CHEMISTRY [2–4]

LARGE RINGS (1933–47)

The work of Ruzicka during 1926–33 on the active principles of the perfume derived from musk and civet established the existence of stable ring systems of more than six carbon atoms. Ruzicka prepared cyclic ketones of 6–18 carbon atoms and noted that the yield was minimum in the region of ten carbon ring systems. In 1933, Ziegler published his first paper on the subject with Eberle and Ohlinger on the synthesis of large carbon ring systems, which later became known as the 'Ruggli–Ziegler dilution principle' [5]. In 1912, Paul Ruggli had suggested that such a synthesis might be performed at high dilution since the chief obstacle to the formation of large ring compounds was the interference from the competing polymerization reaction. Ruggli's views had received scant attention. For the utilization of the dilution principle in the preparation of large ring ketones, it was necessary to employ a cyclization reaction which could be conducted in a homogeneous liquid phase with all the reactants in the solution. Ziegler developed this idea and worked out a simple adaptation of the Dieckmann condensation reaction using α, α-dinitriles (Figure 2). Ziegler

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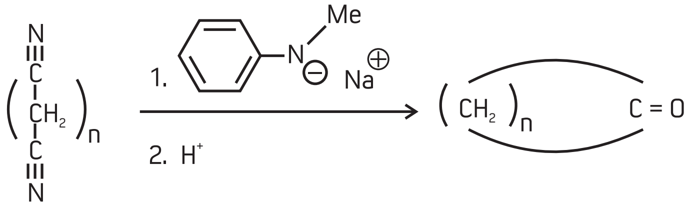
developed this process as a general method and was able to obtain 60–80% yields in the synthesis of rings containing 14–33 carbon atoms, in contrast to the small yields obtained by Ruzicka.

FIGURE 2. ZIEGLER–RUGGLI CONDENSATION.



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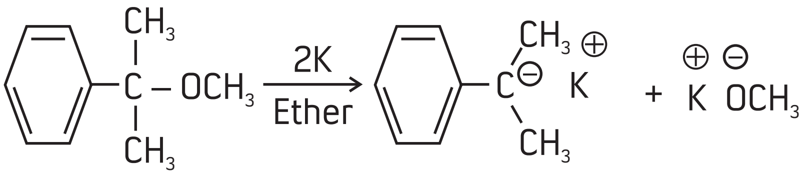
CHEMISTRY OF TRIVALENT CARBON (CARBON FREE RADICALS) (1923–50)

In 1900, Gomberg showed that hexaphenylethane dissociated into triphenylmethyl free radicals [6]. In 1923, Ziegler began to study the factors that determine the dissociation of substituted arylethanes into radicals and asked whether the dissociation was influenced by steric factors or by the electronic character of the substituents attached to ethane. In a series of publications between 1923–50, Ziegler and his co-workers reported a systematic study of the effect of substitution in hexaphenylethane on the dissociation equilibrium. They synthesized a range of substituted ethanes and studied their dissociation into radicals. Determination of the dissociation process with aliphatic substituents proved difficult because the resulting radicals underwent spontaneous disproportionation. But the problem was resolved by a study of the reaction of undissociated ethane and radicals with halogens, oxygen, nitric oxide, and quinones. Ziegler went on to study the rate of dissociation of hexaphenylethane by measuring its rate of combination with nitric oxide. Activation energies for dissociation were determined for a wide range of derivatives, and the rates were measured in a variety of solvents. The latter measurements showed that the rate never varied by more than a factor of 2 with the change of solvent. This led Ziegler to the general conclusion that the dissociation equilibrium constant was not affected by the nature of the solvent. The studies illustrated the wide applications of physical methods to the problems of organic chemistry. For example, Ziegler made detailed measurements of the absorption spectra of hexaphenylethane in different solvents and quantitatively determined the degree of dissociation. He observed that iodine, unlike bromine, does not react with the undissociated hexaphenylethane but reacts very rapidly with the radical. In a specially designed apparatus, he determined the rate of disappearance of iodine colorimetrically by photographically recording the optical extinction coefficient of the reaction mixture at short intervals. The reactions with oxygen were also used to measure the rate of dissociation. Ziegler and co-workers showed that the peroxide formed by the reaction of the radicals with oxygen was a very effective catalyst for bringing about the autoxidation of aldehydes and olefins.

FIGURE 3. SYNTHESIS OF CUMYL POTASSIUM.



> *"In a series of publications between 1923–50, Ziegler and his co-workers reported a systematic study of the effect of substitution in hexaphenylethane on the dissociation equilibrium."*

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In this phase of his career, Ziegler showed his inclination towards using physical methods to probe the mechanism of organic reactions. He was one of the earliest founders and practitioners of the discipline of 'physical organic chemistry'.

ORGANO-ALKALI METAL COMPOUNDS (1932–50)

During his studies on the preparation of substituted arylethanes, Ziegler discovered that cumyl methyl ethers could be cleaved by metallic potassium to yield cumyl (2-phenylisopropyl) potassium salt and potassium methoxide (Figure 3) [7] [8]. This was the beginning of his intense foray into the chemistry of carbanions. He observed that the deep red color of cumyl potassium in ether rapidly changed to a deep yellow upon the addition of stilbene. This marked the discovery of the addition reaction of an organometallic compound (incipient carbanion) to a C=C (carbon-carbon double bond). He further showed that cumyl potassium could also add to 1, 1-diphenylethylene (Figure 4). Those familiar with handling organo-alkali metal compounds will realize the extent of experimental skills that Ziegler brought to bear on the preparation and use of such reactive organometallic compounds. Ziegler could soon explain the mechanism of polymerization of butadiene by metallic sodium, a reaction that was already being studied elsewhere as a method of making synthetic rubbers. By adding more and more butadiene to the deeply red-colored solution of cumyl potassium, the color rapidly changed, with the first mole of butadiene to a light orange, and with more butadiene, to paler and paler yellows. He attributed this observation to the polymerization of butadiene by successive addition of the monomer.

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During his time in Heidelberg, Ziegler became interested in comparing the reactivity of various alkali metal compounds. The method of ether cleavage was suitable for making sodium and potassium derivatives but did not work with lithium. He had explored the preparation of organolithium compounds using dialkyl mercury but was not satisfied with this method. In 1932, Ziegler and Colonius showed that n-butyllithium could be prepared by the reaction of n-butyl chloride with lithium metal in benzene at 35 °C in quantitative yield (Figure 5) [9]. However, attempts to distill butyllithium under high vacuum resulted in the lithium alkyl decomposing into lithium hydride (LiH) and 1-butene. This experimental failure would lead to some unexpected consequences in later years.

FIGURE 4. ADDITION OF AN ORGANOMETALLIC COMPOUND TO A DOUBLE BOND.

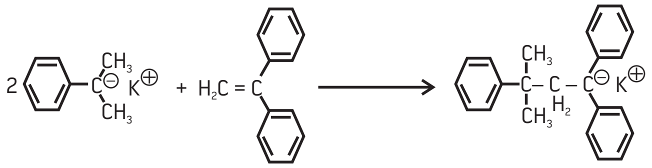

FIGURE 5. PREPARATION OF ORGANOLITHIUM COMPOUND.

$$\text{n-BuCl} + \text{Li} \xrightarrow[\text{Benzene}]{35°\text{C}} \text{n-BuLi} + \text{LiCl}$$

Ziegler diligently pursued his work on the polymerization of unsaturated hydrocarbons by alkali metals and alkyls. Through ingenious experiments, he showed that no free radicals are involved in the polymerization of butadiene. He invoked the intermediacy of organometallic species, which we now understand as carbanions in the form of ion pairs. He showed in 1939 that butadiene could be polymerized in a 1, 2- mode or 1, 4- mode, depending on the experimental conditions and the nature of alkali metal. These studies were truly path-breaking, eventually leading to the industrial processes for the anionic polymerization of dienes in 1954, and ultimately resulting in the discovery of 'living anionic polymerization' of styrene using alkyl metal complexes by M Szwarc in 1956 [10]. The observation that organolithium compounds often function as 'super Grignards,' their ability to metallate other compounds, the famous lithium-halogen exchange, and the role organolithium compounds play in aryne chemistry, are among some of the most striking outcomes of Ziegler's work.

ORGANOALUMINUM COMPOUNDS (1949–60)

Ziegler observed that ethyllithium was more thermostable than n-butyllithium. Attempts to distill ethyllithium also yielded decomposition products, namely, ethylene and lithium hydride. Surprisingly, Ziegler and his co-workers detected a small amount of butene in the gas phase, which they quickly interpreted as a product of addition of two molecules of ethylene. Systematic examinations established that lithium alkyls react with ethylene under pressure and high temperatures to form longer chain alkenes. In Ziegler's own words, and I quote, "It is evident that this addition of ethylene to lithium alkyls is probably the simplest and at the same time the most effective way of lengthening the chain using organometallic reagents. When starting with any lithium alkyl having an even number of carbon atoms, then alkyl chains with an even number of carbon atoms are obtained, while starting with lithium alkyl compounds having an odd number produces alkyl chains with an odd number of carbon atoms." Unfortunately, lithium hydride reacted sluggishly with ethylene. So, Ziegler turned his search to another metal

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hydride, which would rapidly add to ethylene. He found that aluminum hydride (AlH_3) would add smoothly to ethylene to form aluminum alkyls of higher carbon numbers, a reaction he called the 'Aufbau (chain growth) reaction' (Figure 6) [11]. The key to this discovery was the use of neat organoaluminum compounds, unlike earlier workers, who had used aluminum alkyls in ether solvents. We now understand that aluminum alkyls in ether form stable Lewis acid-base complexes, which are inert.

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The discovery of Aufbau reaction opened the door to several industrial applications. Under appropriate conditions, using ethylene and aluminum, one could produce a range of higher α-olefins with carbon numbers 4–30, produce linear alcohols by oxidation of the intermediates or produce straight-chain unbranched paraffin.

However, there was an impediment. Unlike organometallic compounds, aluminum alkyls were difficult to prepare. The reaction of aluminum with ethyl bromide to give ethylaluminum sesquibromide – an equimolar mixture of diethylaluminum bromide and ethylaluminum dibromide – was known, but ethyl bromide was expensive. Ethyl chloride on the contrary was cheap, but does not react under similar conditions. Ziegler and his students discovered that the reaction of aluminum with ethyl chloride could be catalyzed by the sesquibromide prepared in situ. One should admire the skills and courage of his students who demonstrated that organoaluminum compounds, which are pyrophoric[1] and explode in water could be handled safely on a large scale with appropriate care. Sesquichloride, which was later to play a role in the development of the Ziegler catalysts, had to be dehalogenated to obtain triethylaluminum. Metallic sodium was found to be the best material for doing this; when pieces of sodium metal are added to ethylaluminum sesquichloride at around 170 °C, the sodium takes up the chlorine, aluminum is precipitated, and triethylaluminum is formed. By 1952, triethylaluminum was being synthesized in the pilot plant of Kaiser Wilhelm Institute on a 20 kg batch scale – a remarkable achievement in taking difficult chemistry from the laboratory to pilot scale production in less than three years (Figure 7).

On 14 May 1952, Karl Ziegler gave the first comprehensive report of his discovery under the title 'Novel Catalytic Conversion of Olefins'. On 19 May, he gave a lecture on 'Organoaluminum Synthesis in the Field of Olefinic Hydrocarbons' at the annual meeting of the Gesellschaft Deutscher Chemiker (GDCh, German Chemical Society). In the audience, hearing this lecture were two gentlemen, Professor Giulio Natta from Italy and Professor Robert Robinson from the UK. Both were distinguished chemists with deep connections with the industry in their respective countries, a fact that was to have far-reaching consequences in the development of industrial applications of organoaluminum chemistry.

The world currently produces more than 0.5 million tons of organoaluminum compounds. In addition, more than 4 million tons

FIGURE 6. AUFBAU REACTION (STATISTICAL DISTRIBUTION OF - OLEFINS WITH CARBON NUMBERS RANGING FROM 4–30).

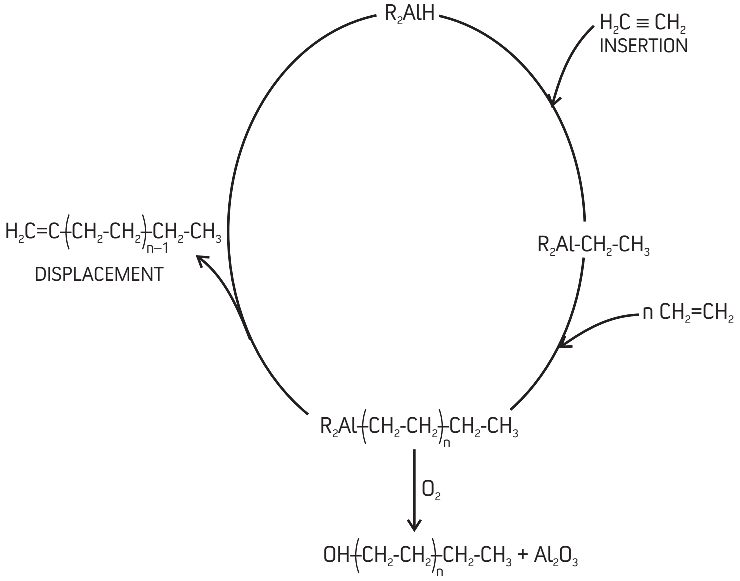
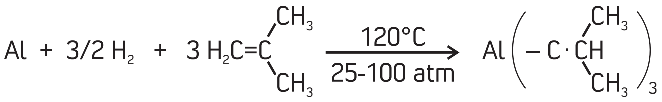


FIGURE 7. PREPARATION OF ORGANOALUMINUM COMPOUNDS.

$$Al + 3/2\,H_2 + 3\,H_2C{=}CH_2 \xrightarrow[25\text{-}100\text{ atm}]{120°C} Al(C_2H_5)_3$$



$$Al + 3/2\,H_2 + 3\,H_2C{=}C(CH_3)_2 \xrightarrow[25\text{-}100\text{ atm}]{120°C} Al\left(-C\cdot CH(CH_3)_2\right)_3$$

$$2\,Al\,(C_2H_5)_3 + AlCl_3 \longrightarrow 3\,(C_2H_5)_2\,AlCl$$

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[1] *Tend to ignite spontaneously in air.*

of α-olefins and linear long chain alcohols (detergent alcohols) are produced using Ziegler's Aufbau chemistry.

METAL-CATALYZED LOW-PRESSURE POLYMERIZATION OF ETHYLENE (1953–60) [12]

In early 1953, one of Ziegler's students, Erhard Holzkamp, while attempting to repeat the Aufbau reaction found that in one particular instance when triethylaluminum was made to react with ethylene, instead of obtaining the expected higher alkenes, he consistently obtained butene-1. This was an anomalous observation and unexpected. It was soon realized that dimerization occurred because of trace nickel impurity in the metal reactor. This was the beginning of a new chapter in organometallic chemistry.

Ziegler recognized the value of this serendipitous discovery. Butenes were not available from refinery operations, and hence this method provided easy access to four carbon olefins. However, several attempts to repeat this experiment failed.

The credit of resolving this mystery goes to Ziegler's keen mind and his quality of not overlooking any stray observations in the laboratory. It was soon found that highly purified ethylene resulted in Aufbau reaction, whereas, ethylene containing small amounts of acetylene as impurity resulted in selective dimerization of ethylene to butane-1! Traces of acetylene stabilize the nickel complex formed in situ. Thus began a new chapter in organometallic chemistry, namely, the 'organonickel chemistry' and its applications.

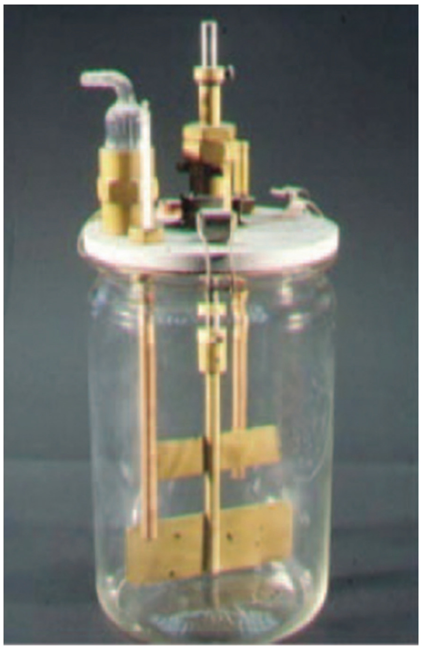
"The world currently produces more than 0.5 million tons of organoaluminum compounds. In addition, more than 4 million tons of α-olefins and linear long chain alcohols (detergent alcohols) are produced using Ziegler's Aufbau chemistry."

In May 1953, Ziegler told his student, Holzkamp, to carry out experiments with chromium compounds to see whether metals other than nickel had a similar effect. Initially, these experiments proceeded without a clear direction, since in addition to olefins, small amounts of solid products (which was possibly polyethylene) were obtained. Ziegler asked another student, Heinz Briel to begin a systematic investigation of the entire Periodic Table to see if there were any other metals that were equally effective! Experiments using the acetylacetonates of chromium, manganese, vanadium, and platinum did not produce any meaningful results. Heinz Briel performed a historic experiment on 26 October 1953, when he reacted ethylene with zirconium acetylacetonate in the presence of triethylaluminum. He found that at 100°C and 100 bar pressure, 38 g of a 'hard paraffin'(a white product) was formed that could be compressed into a sheet. There was intense excitement in the laboratory. Ziegler realized that if nickel is excluded, ethylene indeed could be polymerized to high molecular weight polyethylene in the presence of organoaluminum and a transition metal salt. It was important to systematically develop the sensational results obtained by Heinz Briel as rapidly as possible so that they could be patented. This task was assigned to Heinz Martin, who had already been working on the preparation of polyethylene, although from a different direction. Heinz Briel's experiments with titanium tetrachloride as the transition metal component in combination with triethylaluminum showed that titanium catalysts are considerably more efficient than zirconium. He observed a highly exothermic reaction, a rapid fall in pressure in the autoclave, and the only product was high molecular weight polyethylene. With the help of further variation in the catalyst, Heinz Martin finally achieved the so-called 'normal pressure polymerization', which he was able to carry out in a large glass reactor (Figure 8). Ziegler's thirty years of unrelenting quest on what lies at the core of the unique stability of C-C bonds had yielded him bountiful rewards. His catalysts were able to convert a simple molecule of ethylene (a monomer, containing one π bond) into polyethylene (a polymer containing a limitless number of C-C σ bonds) (Figure 9)!

"Heinz Briel performed a historic experiment on 26 October 1953, when he reacted ethylene with zirconium acetylacetonate in the presence of triethylaluminum."

FIGURE 8. THE GLASS REACTOR IN WHICH THE FIRST SAMPLE OF POLYETHYLENE WAS SYNTHESIZED.

(THE REACTOR IS ON DISPLAY AT THE MAX-PLANCK-INSTITUT F¨UR KOHLENFORSCHUNG AT MULHEIM, SOURCE: [12(A)], COURTESY ATTRIBUTED TO: G FINK).



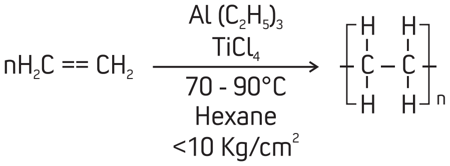
> *"Ziegler realized that if nickel is excluded, ethylene indeed could be polymerized to high molecular weight polyethylene in the presence of organoaluminum and a transition metal salt."*

On 17 November 1953, Karl Ziegler submitted a patent application to the German Patent Office that he had drafted himself. The inventors were Karl Ziegler, Heinz Briel, Erhard Holzkamp, and Heinz Martin. The title of the German patent number 973,626 was, 'A Process for Preparing High Molecular Weight Polyethylene' (Figure 10), and its exemplary claim read as follows:

"A method of preparing high molecular weight polyethylene using aluminum trialkyls as catalysts, characterized by bringing together ethylene at pressures greater than 10 atmospheres and temperatures above 50°C with mixtures of aluminum trialkyls and compounds of the metals of groups IVa to VIa of the Periodic Table with the atomic numbers 22 to 74 (namely titanium, zirconium, hafnium, niobium, tantalum, chromium, molybdenum, and tungsten)."

It is worth noting that Ziegler did list most of the elements in the Periodic Table in his claims! However, the apparent limitation of the claim to ethylene was to cause the institute considerable problems in later years. Karl Ziegler only claimed what had been demonstrated experimentally. Although Heinz Briel had already experimented with propylene, he had not been able to isolate any polypropylene, a material that was not yet known. Ziegler's patent would cause a revolution in the chemical industry and within a short time, provide a strong impetus to basic research in organometallic chemistry and catalysis around the world, giving birth to the new industry of polyolefins.

FIGURE 9. SYNTHESIS OF LINEAR POLYETHYLENE.



$$nH_2C == CH_2 \xrightarrow[\substack{70 - 90°C \\ \text{Hexane} \\ <10\ \text{Kg/cm}^2}]{\substack{Al(C_2H_5)_3 \\ TiCl_4}} \left[-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - \right]_n$$

FIGURE 10. THE FIRST PAGE OF THE HISTORIC MULHEIM PATENT.

BUNDESREPUBLIK DEUTSCHLAND

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 973 626

KLASSE 39c GRUPPE 25

INTERNAT. KLASSE C08f

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

Verfahren zur Herstellung von hochmolekularen Polyäthylenen

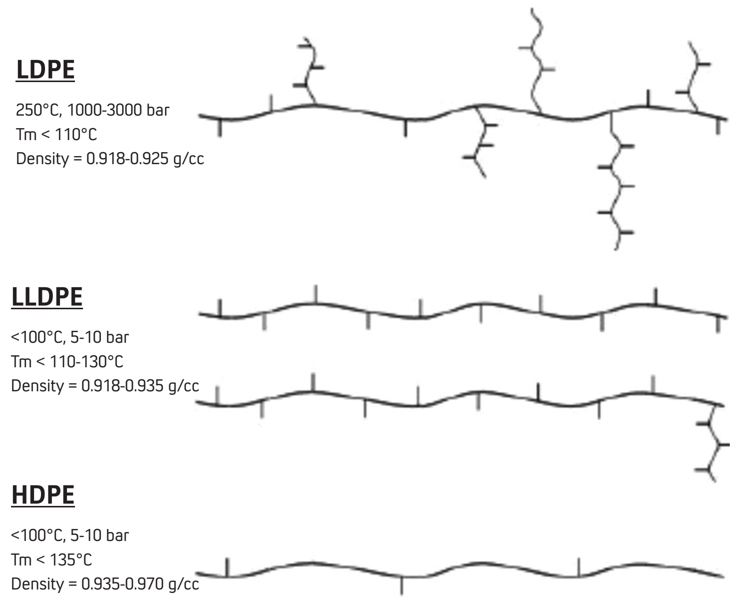
The sensational news spread like wildfire around the world when Karl Ziegler first reported the low-pressure polymerization of ethylene at the IUPAC Congress in Zurich on 22 July 1955 [13,14]. Ironically, Giulio Natta also announced at the same conference, the stereospecific polymerization of propylene to isotactic polymers with the aid of Ziegler's catalyst, without however, disclosing the nature of the catalyst. The manner in which Natta beat Ziegler in the race to polymerize propylene is a separate story. Natta did not discover the catalyst to perform this reaction; he only refined Ziegler's catalyst to polymerize propylene, and he admitted so.

The story of metal catalyzed olefin polymerization began with the Group 3/4 metals in 1954. Since then, the journey has traversed the entire first and several second row metals from Group 3 (Sc) to Group 11 (Cu). Every metal has made a distinctive contribution to the epic saga of polyolefins in terms of new properties and applications fulfilling the needs of humankind. The excitement continues unabated to this day [15].

FROM EXPLORATION TO EXPLOITATION: THE JOURNEY OF POLYETHYLENE

Ethylene became abundantly available as a two-carbon feedstock at the end of World War II – a product of petrochemical and refinery processes. Chemical reactivity of

FIGURE 11. TYPES OF POLYETHYLENE (- INDICATES A METHYL GROUP).



ethylene became a subject of intense study in many parts of the world. Eric Fawcett and Reginald Gibson, working at the Imperial Chemical Industries (ICI), England, accidentally found that upon applying extremely high pressure (several hundred atmospheres) to a mixture of ethylene and benzaldehyde, a white waxy material was produced which was recognized as polyethylene. It was soon understood that the reaction had been initiated by trace oxygen contamination in the apparatus. This reaction was found to be a radical initiated polymerization, and due to the occurrence of several inter- and intra-molecular radical backbiting reactions[2], the polymer was found to have many branches, both short and long chain. Polyethylene so produced had densities between 0.910–0.940 g/cm^3 and were called ‘low density polyethylene’ (LDPE). The conditions of polymerization were severe, with temperatures ranging from 180–250°C and pressures exceeding 1000 bar. Commercial manufacture of polyethylene commenced in 1939.

“[2]A backbiting reaction is one in which a growing free radical at the end of a polymer chain ‘pulls off’ a hydrogen intra-molecularly from a methylene group located in the same chain or inter-molecularly from a methylene group located in another chain. The consequence of this reaction is the generation of a new free radical, either in the same chain in another location or in another polymer chain and the termination of the original growing chain. These new free radical sites can add more ethylene and continue to grow. However, these radical sites are located on secondary carbons. Growth of polymer chains from a secondary carbon radical leads to long chain branching.”

The commercial impact of the chemistry and the process discovered at Mulheim was not lost on Ziegler. Apart from the fact that his catalysts could polymerize ethylene at much lower temperatures and pressures, the polyethylene so produced had some unique structural features. Since the process was not a radical process, the polymer essentially had a linear structure. This was reflected in the higher densities of the polymer, ranging between 0.945–0.970 g/cm^3. Polyethylene with such a linear structure is called ‘high density polyethylene’ (HDPE). HDPEs have distinct physical properties from LDPEs. Today, industries produce a range of polyethylene with densities varying from 0.918–0.970 g/cm^3 to suit diverse consumer needs (Figure 11).

In 1954, Ziegler started granting non-exclusive license to anyone who was interested in exploiting his discoveries. The fact that he was both the Director of the institute and the Managing Director of Studiengesellschaft Kohle GmbH, which was the trustee for the institute, was a great advantage. The licensees who thronged to Mulheim recognized Ziegler as a skillful negotiator with a keen business acumen. The business of licensing flourished, and between 1953 and 1990, no less than 80–90 contracts were signed, spread over 20 different countries. It is interesting to note that the licensing income guaranteed the institute complete financial independence from the Max Planck Society for more than forty years. Thus, the economic benefits continued to flow for more than twenty years after Karl Ziegler retired from the directorship of the institute. However, the licensing activity also resulted in numerous infringements of the institute’s patents, which led to several lawsuits particularly in the USA, which the institute had to defend at a high cost.

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Heinz Martin, one of the coinventors of polyethylene was engaged full-time in looking after the interests of the institute – the granting of licenses as well as the defense of patent rights. He was ideally equipped, both as a scientist and as an experienced insider of the patents world. Heinz Martin has provided a fascinating account of the journey of commercially exploiting the inventions made at Mulheim, the trials and tribulations, in his book, Polymers, Patents, and Profits, published in 2007 [16]. In the present era when the academia is waking up to the potential of creating wealth out of intellectual property, the documented experience of one of the pioneers of this effort is worth a careful study.

The first manufacturing plant, set up by Hoechst, to produce 10,000 tons of HDPE per annum, went on-stream in Germany in 1957, less than four years from the first laboratory observation. This time frame of conception to commercialization is unprecedented in the history of industrial chemistry! In 2016, the world produced and consumed close to 100 million tons of linear polyethylene and its copolymers, at an estimated total market value of 150 billion USD, all produced using Ziegler's chemistry.

"The first manufacturing plant, set up by Hoechst, to produce 10,000 tons of HDPE per annum, went on-stream in Germany in 1957, less than four years from the first laboratory observation."

SERENDIPITY OR SYSTEMATIC WORK?

A cursory reading of Ziegler's work may lead one to believe that he was 'lucky' most of the time, stumbling upon important discoveries mostly 'by chance.' Serendipity has a role in science, but chance only favors a prepared mind [17]. Ziegler's research progression from large ring compounds to free radicals, organometallic compounds, and finally to polymerization catalysts had a compelling logic. He was constantly striving for a deeper and deeper understanding of the nature of C-C bond forming reactions. The quintessential question that obsessed Ziegler in all his explorations was: What lies at the core of C-C bond stability? The pursuit of an answer to this question led Ziegler, step by step and systematically, from free radical chemistry to his eventual discovery of a practical way of making polyethylene. His research was guided by one experiment after another, performed in a logical sequence. For Ziegler, a keen sense of observation was the most important part of performing experiments. He taught his students never to miss recording any trivial or stray observation, however unexpected it may seem. Diligent pursuit of such trivial observations and search for their explanations led him to his greatest discovery. His work exemplifies the well-known dictum that nature is a hard taskmaster. It reveals its secrets only to those who are diligent and patient. Ziegler's life and work is an unequivocal endorsement of the thesis that crucial discoveries in science can only be made when scientific questions are pursued systematically. The edifice of science has to be built painstakingly, one brick at a time.

"Ziegler's life and work is an unequivocal endorsement of the thesis that crucial discoveries in science can only be made when scientific questions are pursued systematically."

BASIC OR APPLIED RESEARCH? [18–21]

The life and works of Ziegler are relevant even more today when there is a furious debate on how much of science should be directed towards meeting specific end goals, and how much of it should be unfettered and left to the best judgment of the individual scientist. Ziegler was driven by the philosophy that in-depth knowledge alone can lead to new applications. In his own words, and I quote, "What has guided my research has been solely the wish to do something that gave me joy, that is a joy from finding, somehow or somewhere, something really novel. At least at the outset, the only thing of value aimed for is an accretion of knowledge, rather than new applications." In Ziegler's work, we do not find a dichotomy between basic and applied research.

Science is an enterprise pursued by individuals with diverse personalities. While some find joy in discovering new knowledge, others find happiness in applying knowledge for the benefit of the society. From these different motivations of scientists have emerged basic and applied research. There are often debates that expound the virtues of one or the other type of research. But history of science shows that it is constraining and harmful to make a strict distinction between basic and applied research, and very often one leads to the other. Ziegler did not set out to solve any particular problem relevant to industrial chemistry. Yet, he saw no dichotomy between high-quality basic science and clever and ingenious applied research. He understood that new insights into chemistry would have novel technological applications, and both endeavors demand imagination and intellect. He firmly believed that scientific inquiry should not be restricted by shortsighted timelines and narrowly defined objectives. Ziegler's life teach us that new knowledge is generated when there is a compelling desire to understand and when intellectual pursuits are free from the constraints of defined applications and set targets.

> *"What has guided my research has been solely the wish to do something that gave me joy, that is a joy from finding, somehow or somewhere, something really novel." – K Ziegler*

> *"History of science shows that it is constraining and harmful to make a strict distinction between basic and applied research, and very often one leads to the other."*

These issues gain even more significance in the present times when governments and funding agencies evaluate research from the touchstone of relevance. Curiosity-driven basic research is under pressure to justify itself; it is endangered and vulnerable. Current global policy tends to measure the value of research solely on its immediate applications – whether the studies address a social problem or can deliver a marketable product in the foreseeable future, preferably within a few years. Scientists are expected to solve societal problems in the shortest possible time frame. It is becoming increasingly difficult to convince that in science, the judgment of relevance can be made only in the long-term and in hindsight.

LESSONS FROM ZIEGLER'S LIFE

Ziegler's life and work teach us many lessons that are important to both scientists and those aspiring to be scientists. I enumerate a few of them here:

1. Knowledge – in-depth and breadth – is most important.
2. Systematic work yields the highest dividends in research.
3. Experiments and observations are more important than mere theories or hypotheses.
4. Pay attention to every small and stray observation, however trivial and counter-intuitive it may seem. Generally, it is the anomalies and not the data that perfectly fits a preconceived notion, that lead to new discoveries.
5. We have to learn to recognize the general significance of a new and unexpected result, and then follow it up systematically and diligently.
6. Once you recognize something of utility in your work, pursue it to its logical conclusion.

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