Chapter 2
Polyolefins—The History and Economic Impact

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2.1 Introduction

2.1.1 Definition

Olefins (from the French oléfiant, "oil-forming"),[1] or alkenes, are hydrocarbon molecules with at least one double carbon–carbon bond. Alpha (α-)olefins are alkenes with a double bond at the first (alpha-) carbon. Polyolefins are polymer molecules, made using either free-radical or ionic initiators or inorganic (metal oxide) or organo-metallic catalysts, to open the reactive double-bonds in these olefins, in an addition (chain-growth) polymerization reaction. These polymerisation processes produce essentially linear high molecular weight thermoplastic polymers, which are now the main topic of this chapter.

These polyolefin polymers, since their commercialization around 80 years ago, are now (2013) the major fraction (62 %) of the plastic materials which have transformed modern life [1]. In 1960, they comprised only 20 % of global polymer demand, but already by 1995, this had reached 60 % [2].

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[1]Because olefins combine readily with halogens to form oily liquids

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No other major material has appeared on the scene and achieved such a dominant and ubiquitous place in such a short time. As new materials, polyolefins have introduced new possibilities and benefits at attractive price points. Their annual growth rate remains exponential.

Polyolefins are used in every sector of life and are processed by every significant polymer processing technology. Whereas they are commonly perceived as commodity polymers, and their vast production and consumption volumes are testimony to this, polyolefins can also be speciality and outstanding niche materials, with unique properties and features.

2.1.2 Scope

In this chapter, we seek to demonstrate the broad and enormous economic and commercial impact of these polyolefins, by considering a number of dimensions that contribute to economic impact.

The commercial and economic impact of polyolefins is inextricably linked with the discovery, recognition, or development of properties and performance that creates value. Thus, we integrate the technical application and market development of polyolefins in our discussion.

We start with a historical perspective on how the industry evolved from the early discoveries in research laboratories in Germany and England to become a global industry of almost 170 million tons and value around $200 billion, in just over 80 years.

2.2 Polyolefins: The History and Economic Impact

2.2.1 Polyolefin Elastomer

Strictly speaking, the first high molecular weight polyolefin to be commercialized was a homopolymer of isobutylene. This polyisobutylene (PIB) was first developed by IG Farben [***I****nteressen-****G****emeinschaft* ***Farben****industrie AG*] in 1931 using a boron trifluoride catalyst at low temperatures. We could note that the monomer, isobutylene, was discovered by Michael Faraday just over 100 years before, in 1825. PIB of medium and high molecular weight is sold under the trade name Oppanol B, a core business for BASF to this day. BASF acquired the competing Vistanex PIB business of ExxonMobil in 2003. BASF have 4 plants that make PIB, including the 18,000 ton plant at Ludwigshafen. Polyisobutylene has a low T_g (−73 °C) and does not crystallize. PIB homopolymers of high molecular weight (100,000–400,000 or more) are therefore polyolefin elastomers, not (thermo)plastics, and so fall outside of our scope. They are tough extensible rubber-like materials over a wide temperature range, with a characteristically low density of polyolefins 0.913–0.920, low permeability, and excellent electrical properties.

Polyisobutylene is used as the base of chewing gum, in adhesives, sealants, roofing, coatings, protection for optical fibre bundles, and electrical cable sheathing. In 2017, the overall polyisobutylene production is anticipated to reach 1.2 million tonnes [3].

Lower molecular weight polyisobutylene is sold by BASF as Glissopal®, as an important intermediate for the manufacture of additives for fuels and lubricants, made in plants in Antwerp and Ludwigshafen of capacities 100,000 and 40,000 tons per annum (tpa), respectively.

Polyisobutylene was later developed into butyl rubber [IIR] in 1937, by researchers William J. Sparks and Robert M. Thomas, at Standard Oil (later, ExxonMobil) by copolymerizing about 2 % of isoprene into polyisobutylene, to provide the unsaturation for vulcanization (cross-linking with sulphur). This butyl rubber was commercialized in 1943, and in 2016, the global capacity for IIR is expected to be 1.6 million tons, with 6 players. ExxonMobil has a 40 % market share. Since butyl rubber has outstanding permeability, tire inner tubes were the first major use of butyl rubber, and this continues to be a significant market today.

This important segment (PIB, and its derivative IIR) has clear economic impact through its unique and diverse applications and performance. Together, they total around 2.8 million tons per annum, generating a revenue of around $4bn. This segment was included here, so as to provide the full picture on the development of polyolefins, but is not a part of the commonly recognized polyolefin industry that we now turn to.

2.2.2 Polyethylene (PE)

Our story really begins with polyethylene. The first record of this word appears in the work of the French chemist Pierre Eugène Marcellin Berthelot, who reported in 1869 on his studies of ethylene exposed to boiling alkali, in which he described the olefin fraction boiling at 280–300 °C as “polyethylene” [4]. *These may have been ethylene polymers, or perhaps oligomers, but they were not solids!*

More than 60 years later, we see the first preparation of polyethylene by Prof. Marvel, a discovery that languished, and then 3 years later, the serendipitous discovery of (solid) thermoplastic polyethylene in 1933, in the research laboratories of ICI, and its commercial production by 1938.

In 1930, Professor Carl Shipp “Speed” Marvel, just starting as a technical consultant with DuPont, had assigned a graduate student [5], to prepare alkylated arsenic compounds, from tetra-ethyl-arsenium bromide and butyl lithium. One experiment involved passing ethylene gas through a solution of n-butyl lithium in a mineral oil at elevated temperature. The white powder that resulted was the first solid linear polyethylene in excellent yield by direct addition polymerization with an organo-metallic catalyst under very mild conditions. It is supposed that DuPont was both preoccupied with a number of commercially interesting polymers (including nylon, neoprene, acrylics) and that the commercial possibilities of a linear polyethylene were not seen [6, 7].

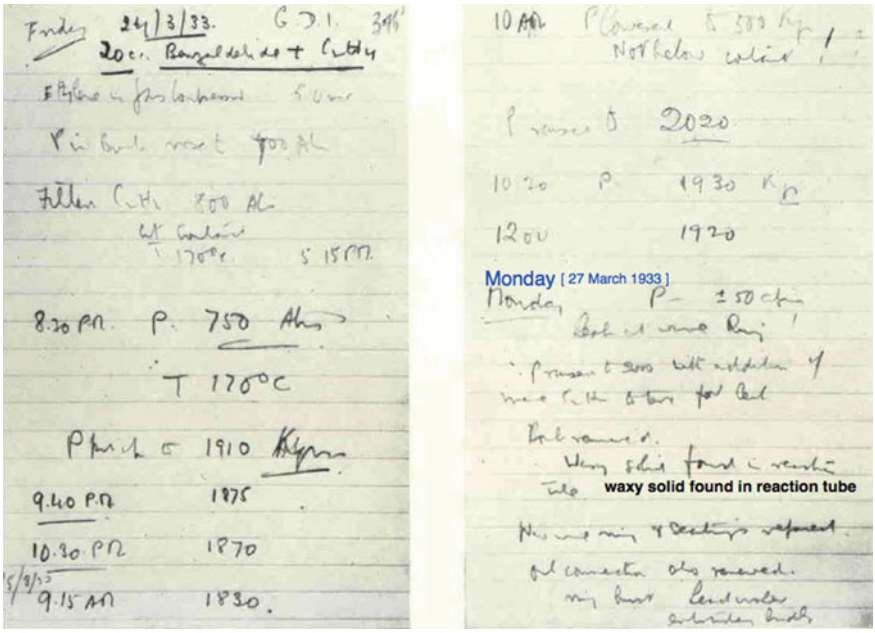


Fig. 2.1 Original laboratory notebook observation recorded by Reginald Oswald Gibson at ICI laboratories describing the waxy solid (PE) found in the reactor tube [8]

It all started with a chance observation on 27 March 1933, by Eric William Fawcett and Reginald Oswald Gibson of ICI Research in Winnington, Cheshire, England, who were investigating the effects of very high pressures—above 1000 atmospheres—on chemical reactions [8]. They had started an experiment on Friday 24 March, to react ethylene and benzaldehyde (one of 50 reactions suggested by Sir Robert Robinson, consultant to ICI, Nobel Prize in Chemistry 1947) at 170 °C and a pressure of 1900 atmospheres. On Monday 27 March, 1933, the reactor "bomb" was dismantled and Fawcett observed that the tip of the steel U-tube was coated with a waxy material. Gibson recorded in his rough notebook: "*Waxy solid found in reaction tube*" (Fig. 2.1).

Fawcett collected 0.4 g of this wax, had it analysed, and an empirical formula of CH_2 was found, with a molecular weight of at least 3700. He internally reported this (7 April 1933) as "probably polymerized ethylene". From this 0.4 gram isolated by Gibson and Fawcett in 1933, polyethylene has grown in 80 years into a global industry producing over 80 million tons per year, the largest volume thermoplastic in the world (2013 figures). This is the remarkable growth story that we proceed to outline.

It is now thought that the ethylene that Fawcett and Gibson used may have contained enough oxygen to initiate the free radical polymerization of the ethylene under this pressure [9]. This (what was originally called high-pressure PE, and what we now call low density) polyethylene was and is made by a free radical high-pressure polymerization. When "improved facilities" were available in the ICI

research laboratories, this experiment, with ethylene alone, was repeated, on 20 December 1935. This time, 8.5 g of solid was prepared.

We should not forget that this discovery of polyethylene was at a time when polymer science was at the very beginning. On 26–28 September 1935, the Faraday Society held the first major conference on polymer science in the UK in Cambridge; Fawcett attended [8]. Hermann Staudinger (1953 Nobel Laureate in Chemistry) presented a paper on the first day in which he described ethylene as a stable compound which polymerizes with difficulty, giving only low molecular weight mixtures of hydrocarbons. In the discussion on Staudinger's paper, Herman Mark, the chairman of the conference, himself invoked some theoretical arguments to explain why ethylene does not polymerize. Then, Fawcett got up and told the Conference that he had actually made a solid polymer of ethylene, with a molecular weight of about 4000, by heating ethylene to 170 °C at about 2000 bar. This disclosure "elicited no reaction from the people present, the cream of England and world polymer scientists", and Staudinger, even when prompted by the chairman, declined to comment. Fawcett was apparently dismissed from ICI for this disclosure [6]. We know that in 1938, Fawcett joined BP Research.

One year after Fawcett's unauthorized statement, the ICI "process for polymerizing ethylene to (technically useful) solid polymers" was formally disclosed in British Patent 471590 (applied 4 February 1936, allowed 6 Sept. 1937) and the related US Patent 2153553 (Polymerization of olefins, Publication date 11 April, 1939 Priority date 4 Feb, 1936 Fawcett Eric William, Gibson Reginald Oswald, Perrin Michael Willcox, ICI Limited).

In November 1937, ICI started up a 9 litre reaction vessel that could produce about 10 tons per annum [tpa] of polyethylene. Continuous operation was not achieved until the first ton of polyethylene was made on 22 December 1938. We might say that the polyolefin industry had begun!

A 100-tpa polyethylene plant was started up in Wallerscote in September 1939, and the second 100-tpa plant was completed in May 1940.

These investments and significant advances in equipment design and reliability were made in parallel with the development of applications for this new material.

In 1936, (later, Sir) Michael Perrin wrote "It is felt that, of a large number of possible uses, attention should first be concentrated on those connected with the electrical industry, where the outstanding insulating properties of Alketh combined with its flexibility in the form of tape and films, and its chemical inertness, would appear to be most promising".[2]

Indeed, the first suggested use for polyethylene came from B.J. Habgood, who had joined ICI from the cable industry: the combination of electrical properties (high dielectric strength, low loss factor, and moisture resistance) and mechanical properties made it suitable as an insulator for trans-Atlantic coaxial telephone cable. The demand at that time was estimated at 2000 tons per annum. It eventually replaced the natural thermoplastic polymer gutta percha (trans-1,4-polyisoprene)

[2]In May 1942 ICI introduced the trademark Alkathene to replace Alketh.

which had been used in cable insulation since 1843, when it was first used to insulate the telegraph lines along the Great Western Railroad.

The submarine trans-Atlantic telegraph cables of 1857, 1858, and 1865 were insulated with gutta percha, which was the prime material for submarine cable insulation for over 80 years, until it was replaced by the new polyethylene. One of the key drivers of the growth of the polymer industry—"material substitution"—had been initiated.

The PE produced at this time by high pressure had a density of 910–920 kg/m^3 and became known as "low-density" polyethylene, once polyethylenes of greater linearity (less branching, so the chains are more easily packed together, giving high (er) density) were developed.

The submarine telephone cable application was the justification for the commercial PE plant, but in fact—with the outbreak of World War 2 in 1939—almost all of the 4000 tons of PE produced between 1939 and 1945 was used to insulate high-frequency radar cables. Commercial distribution of PE in the UK was suspended, secrecy was imposed, whilst PE was used to produce insulation for the coaxial cables of radar sets. Airborne radar, possible because of the compact cables available now with PE insulation, proved to be a critical advantage in the Battle of Britain and the Battle of the Atlantic, helping British supply ships to avoid German submarines. German Admiral Karl Dönitz told Adolf Hitler in May 1943: "What is now decisive is that enemy aircraft have been equipped with a new location apparatus … which enables them to detect submarines and to attack them unexpectedly in low cloud, bad visibility or at night" [10].

Once warfare had ceased in Europe (May 1945) and in Asia (August 1945), the military demand for PE reduced, and the search for modified products and alternative applications started. Another of the key drivers of the growth of the polymer industry—"product and application development"—had been initiated.

Calendered PE sheet (Crinothene) was used for lampshades. Winothene was a low molecular weight PE made for wax applications. Halothene was a chlorinated PE. None of these proved a growth driver for the PE business. However, a major application for PE was found once ICI Plastics started its first 122 cm (48″) film extruder. Today, extruded film (blown film, cast film, extrusion coating) is the major process/application across the main types of PE.

2.2.2.1 "Exceptional Invention"

In October 1929, DuPont signed a "patents and process agreement" with ICI "to exchange scientific and technical information on a routine basis", which was effective until 1948, when the US Department of Justice brought antitrust pressures to bear, and it was cancelled (it was due to expire in 1949 anyway) [11].

DuPont claimed neoprene (1930) and nylon (1934) as "exceptional inventions" and so—within the understanding but not the actual contractual terms of the agreement—did not make early disclosure of these to ICI. Polyethylene was disclosed by ICI to DuPont in September 1933, but later, in 1939, ICI notified DuPont

that polyethylene was an "exceptional invention", so was—likewise—outside of the scope of their agreement.

DuPont started their investigations of high-pressure polymerization in 1936 and by 1940 had developed an improved process for making PE. A 50-ton pilot plant was completed in December 1942, and a 500-ton plant was started up in March 1943 [11].

DuPont had been granted rights to grant non-exclusive sub-licences of the ICI Patents. Union Carbide approached DuPont in October 1942 for a sub-licence, whilst simultaneously contracting to supply the Navy with PE, building a 500-ton PE plant, and then improving the process and product. By the end of the war, Union Carbide had increased their capacity to six times that of DuPont, who were now making 750 tons per annum. Applications were found in extruded film, coated paper, wire and cable insulation, bottles, and pipes.

2.2.2.2 Linear Polyethylene

DuPont had discovered (patent application 739,264, filed 3 April 1947) that a more linear free radical PE—with a density of 0.955—could be made using a specific free radical initiator such as AZDN (azo-di-iso butyronitrile), under very extreme pressure conditions (their patent indicates 5000–20,000 atmospheres). They were unable to convince the patent examiners that this linear polyethylene was a patentable invention. Only after the discoveries from 1951 (publication of the various low-pressure HDPE process patents, outlined below) did this patent USP 2816883 publish. DuPont never pursued this linear polyethylene, because the extreme pressures "greatly exceeded the limits of commercial feasibility" [11].

2.3 Inorganic and Organo-Metallic Catalysts

The next major step, almost two decades after the discovery by ICI of their high-pressure free radical polymerization of ethylene, was the discovery, from 1951, of (metal oxide and organo-metallic) catalysts that produced essentially linear high molecular weight polyethylene (and other polyolefins) under much lower pressures. These catalyst discoveries occurred almost simultaneously and independently in several laboratories in the USA and Europe [12].

We briefly review these discoveries, chronologically, and see how they led to several industrial processes that were the foundation of the significant growth of the polyethylene industry since the 1950s. We then see how this technology was rapidly extended to create the polypropylene industry. The growth of the polyolefin industry in these last 60 years is the story primarily—in terms of volume and impact—of the growth of polyethylene and polypropylene.

Although from our perspective, more than 60 years later, we see polyethylene and polypropylene as quite different polymers and industries, and the commercial value of each of these polyolefin polymers is appreciated, yet from the 1950s perspective of the "new" metal oxide and organo-metallic catalyst syntheses, they

were just outcomes of α-olefin polymerization. That is why the early days of polyethylene and polypropylene and these metal oxide and organo-metallic catalysts are such entwined and convoluted histories.

2.3.1 DuPont "on the Brink of a Tremendously Interesting Field of Polymer Chemistry"

Although from the patent/legal perspective, DuPont is not at the beginning of the chronology, it is described first, because the much earlier work of Prof. Marvel in 1930 might be seen as the starting point of organo-metallic catalyst synthesis of solid polymers and because the work from 1954 at DuPont was specifically derived from an earlier (1943) antecedent at BASF.

In 1954, the exploratory research section of DuPont, a group of about 10 men headed by Dr. Frank Gresham, began to investigate polymers that were of higher modulus than (low-density) polyethylene. To decrease the chain flexibility, they sought to incorporate norbornene as a "bulky" comonomer into the polyethylene chain. One chemist in the group, Nicholas G. Merckling, was assigned to find a suitable polymerization catalyst for this. Merckling found, in his literature review, that Max Fischer of BASF had been issued with a (1953) patent based on his 1943 (during WWII) improvement of a titanium and aluminium chloride catalyst for polymerizing ethylene to low molecular weight liquids. When Merckling pursued this and succeeded in making a higher modulus polyethylene using these catalysts, it was quickly recognized that he had made linear polyethylene by a relatively low-pressure process and that with this new catalyst (Gresham wrote to his boss) "we are on the brink of a tremendously interesting field of polymer chemistry". On 16 August 1954, Merckling filed a patent for the reduced (divalent) titanium catalyst and a process for polymerizing ethylene from 1 – 100 bar.[3] In one example (X), they disclosed a polyethylene of density 0.98, and in another (XIX), a molecular weight too high for the melt flow index to be measured.

2.3.2 Standard Oil of Indiana (later, Amoco)

Alex Zletz of Standard Oil of Indiana (later, Amoco) was actually the first to disclose (patent filed 28 April 1951) the use of a transition metal catalyst for the production of highly linear (what came to be called high density) polyethylene HDPE, using a molybdenum oxide catalyst supported on alumina.[4] The polymer density was 0.96. The purpose and process of their invention is very clearly stated in this patent:

[3]Source: US Patent 3541074.

[4]Source: US Patent 2692257.

> …to provide a relatively low temperature, low-pressure process for the conversion of ethylene-containing gases to high molecular weight resinous or plastic materials.Briefly, the inventive process comprises the conversion of ethylene principally to high molecular weight normally solid polymers by contact with an alkali metal and one or more of the oxides of chromium, molybdenum, tungsten, or uranium, extended upon a support [13].

The management was unsure of the importance of this product, and commercialization was slow. The first plant using this technology went on stream in 1961, in Japan. Three plants were eventually built between 1961 and 1971, but the process had poor economics and was soon "dead". Ironically, the first technology to market, which normally has an advantage, had little economic impact and has no place in the polyethylene technology of today.

2.3.3 *Phillips Petroleum Company*

On 5 June 1951, Phillips Petroleum Company (now Phillips 66, which owns 50 % of Chevron Phillips Chemical) researchers Hogan and Banks were attempting to convert propylene into gasoline (petrol), when they discovered crystalline polypropylene.

This discovery led to the development of a new catalytic process based on chromium oxide, for making both polypropylene and high-density polyethylene (HDPE) in January 1953.[5] This "Phillips (chromium) catalyst" gave a highly linear, very crystalline polymer, of density 0.963, with resultant improved mechanical properties, at low pressure. Phillips invested $50 million in developing this new technology and introduced their Marlex® HDPE in 1956. At the outset, there was only one grade available—with a melt index below 1 (a high molecular weight grade). This did not match with the already diverse market needs, so inventory began to build. It is said that Marlex® was probably "saved" by the Wham-O Company, who in 1958 made their new "craze" product, the HulaHoop, from Marlex® polyethylene tubing—lots of it: over 100 million hoops were made within 2 years. The completely unanticipated demand for Marlex gave Phillips the time necessary to resolve initial production problems and position itself as a prime source of plastic resins. This tremendous contribution by the two Phillips Petroleum scientists was commemorated by the US Postal Service (USPS) in an official stamp that features their photos (Fig. 2.2).

These Phillips discoveries were commercialized rapidly and remain a major process today, in more advanced forms: the Phillips supported chromium catalyst is used to produce some 40–50 % of the world's HDPE. The first plants were brought on stream in 1955 and 1956. However, Phillips management concluded that no one manufacturer could develop the full market potential of the Phillips HDPE and therefore decided to license the process. By 1956, nine companies in seven countries had become licensees.

[5]Source: US Patent 2825721.



Fig. 2.2 US postal service stamp commemorating Phillips Petroleum Scientists Robert Banks and Paul Hogan

2.3.4 Prof. Karl Ziegler

"The Ziegler catalyst was… an unprecedented break-through in … polymer synthesis" [6].

In February 1943, Prof. Dr. Karl Ziegler was invited to be the director of the Kaiser-Wilhelm-Institut für Kohlenforschung (renamed in 1949 the *Max-Planck-Institut für Kohlen-forschung*) in Mülheim an der Ruhr and appointed on 16 April 1943.

There, continuing with organo-metallic chemistry, Karl Ziegler and Hans-Georg Gellert found that triethyl aluminium could react with ethylene by stepwise insertion—what was called the "Aufbau" (building up) reaction—to produce ethylene oligomers and low molecular weight waxes or polymers (up to 100 ethylene insertions).[6]

In early 1953, in the hands of the graduate student Erhard Holzkamp, this established Aufbau reaction unexpectedly took a different course. Instead of oligomers, he obtained a quantitative yield of 1-butene, in addition to unchanged triethylaluminium! It was eventually found that this was due to minute traces of colloidal nickel in the reaction vessel, remaining from previous hydrogenation studies. This finding was later called the "Nickel-Effect". Prof. Ziegler then instigated a systematic investigation of the effect of other transition metal compounds on the Aufbau Reaction [14]. A new graduate student, Heinz Breil, was given the task of carrying out this systematic search.

On 26 October 1953, Breil carried out the reaction which was to revolutionize polymer chemistry: he treated ethylene with triethylaluminium in the presence of zirconium (acetylacetonate). The reaction was carried out under the standard conditions used for the Aufbau Reaction (100 °C, 100 bar) but took a completely different course—a white mass of polyethylene was formed. On 17 November 1953, only three weeks after Heinz Breil's original experiment, Karl Ziegler submitted a 2-claim 4-page patent (for intellectual property, Ziegler characteristically wrote and defended and negotiated himself) to the German Patent Office, claiming a

[6]Source: US Patent 2699457.

method to prepare high molecular weight polyethylene with an organo-metallic catalyst consisting of a trialkyl aluminium species and a transition metal compound.[7]

Karl Ziegler aggressively licensed his invention. In 1954, these agreements earned Karl Ziegler and the Max-Planck Institute for Coal Research a total of almost 9 million Deutsche Marks (compared to the Institute's then annual budget of 1.2 m Deutsche Marks), or $4.5 m at 1954 exchange rates (4.2DEM/$). The Max-Planck Institute for coal research in Mülheim was sustained for more than 40 years [15] on the proceeds of the exploitation of its patent rights dating back to 1953/1954.

However, the licence from Ziegler provided only access to catalyst knowledge, and each licensee had to develop a process. This was in stark contrast to Phillips Petroleum, who provided catalysts and process knowledge as part of their licensing strategy.

The first full-scale low-pressure HDPE plant was erected by Farbwerke Hoechst AG in Germany in late 1955. Plastic Technology reported, in September 1955, that this Hostalen® resin, with a density of 0.94 g/cc, was the talk of the Hanover Industrial Fair in Germany, where it was shown for the first time in applications such as film, pipe, tubing, and moulded household articles. This first Ziegler plant was brought on stream by Hoechst in late 1956 and the second one in 1957 in the USA, by Hercules.

By 1960, US production of HDPE via the Phillips process had reached over 91,000 tons annually, whilst 32,000 tons came from the Ziegler process.

The combination of transition metal halides and aluminium alkyls has remained at the heart of the Ziegler catalyst, and is today the world's most widely employed technology for polyolefin production [16].

2.3.5 *Hercules Powder Company*

Edwin J. Vandenberg describes, as a participant, his own early work in polyethylene synthesis at Hercules, noting retrospectively that his ferrous complex with cumene hydroperoxide in t-butyl alcohol produced what was "obviously the linear high-density polyethylene" that "has become a very important, large volume commercial product" [17]. But his molecular weights were too low for him to recognize the value of this linear polyethylene, and in any event, his process was too poor (low conversion and yield) to be useful. Of course, later, Hercules went on to become the first US company to make polypropylene and became in the 1980s the world's largest producer of PP.

From this brief survey of contemporaneous discoveries on polyolefin polymerization, it is evident that catalysis became a dominant technology factor to consider

[7]Source: German Patent 973626 K. Ziegler.

within 20 years of the discovery of high-pressure (low-density) polyethylene. These various catalysts enabled linear polyethylene of higher density and higher crystallinity and improved mechanical properties to be manufactured, without the extremes of pressure and temperature that LDPE required. These catalysts were moved quickly from the laboratory to industrial plants. We surveyed the catalyst discoveries, with patent applications submitted from April 1951 to November 1953. By early 1956, eight companies had announced the capacity of 172,000 tons to manufacture linear PE. Phillips started in late 1956, most by mid-1958. DuPont delayed manufacturing linear PE until 1960, when it captured a 10 % market share.

2.4 New Entrants

Aggressive investment in production capacity, ahead of demand growth, naturally depressed market prices, as each new entrant sought to gain or maintain market share. These new entrants included companies—such as Phillips Petroleum—moving downstream into the chemical space (as Aramco is now doing, 60 years later) or those from other sectors moving into chemicals for strategic reasons. W.R. Grace was a shipping company, used to lower margins, who found the diversification into the relatively dynamic chemical industry provided attractive returns, even in this competitive situation. In fact, the PE from W.R. Grace ("Grex") was the original material that was used in the HulaHoop craze, before demand outstripped the Grex capacity, and Marlex became the major supplier of the PE tubing.

The creation of the HDPE industry, with so many players, such investment in capacity ahead of demand growth, and the resultant intense competition, meant that by 1970, linear polyethylene was a DuPont venture that was still $20 million in the red [10]—a considerable economic impact.

2.5 LLDPE

In January 1957, DuPont filed for a patent, based on the finding that the incorporation of higher α-olefins in PE[8] improved the product, but for DuPont, it appears that this ethylene copolymer was not really a very attractive venture compared to their other, high-margin proprietary products, like nylon. Although Du Pont of Canada introduced such a process in 1960, worldwide the products remained a small volume specialty until 1978, when Union Carbide announced their Unipol process, and actually coined the name "linear low-density polyethylene" (LLDPE). As we see later, since 1980, LLDPE has continued to increase its importance in the

[8]Source: US Patent 4076698

evolution of the portfolio of polyethylene products, likely to approach 1/3 of the total PE market by the end of this decade.

2.6 Progress in Catalyst Chemistries

The chromium (Phillips) and titanium (Ziegler) catalysts have remained the primary industrial catalysts for HDPE and were dominant for three decades, until the discovery in 1979 by Walter Kaminsky of methylaluminoxane (MAO) as an activator for metallocene catalysts, as this compound was far more capable of ionizing the transition metal compound. These new activated metallocenes (e.g. zirconocene)—alternatively described as single-site catalysts—were now suitable for polyolefin polymerization, up to 100 times more active than Ziegler catalysts, and the monomer insertion time (30 μs) was as fast as enzymatic processes. Kaminsky found that the homogeneous (soluble) nature of these metallocene-based catalyst systems made them "dramatically different from Ziegler–Natta catalysts". Because his catalysts led to lower polydispersities, more uniform incorporation of comonomers, giving different properties and manufacturing processes, he described them as "a revolution in the polymer industry". Metallocene catalysts have particularly found application in LLDPE, but "the resulting improvements in—clarity, strength, and lower hexane extractables—usually come at a higher price, so market penetration has not been as great as was originally predicted" [18]. Latest estimates are that perhaps 10 % of LLDPE is made using metallocene catalysts [19].

The sheer size and value of the polyethylene industry ensure that there is continued research, progress, and development in catalysis, for their potential commercial impact. Although this whole subject is not within the scope of this chapter, we mention a couple of aspects of the progress, which offer the potential to impact this industry. In 1995, DuPont introduced work, carried out with them at the University of North Carolina—via the largest patent application ever in the USA.[9] They disclosed what are described as "post-metallocene" catalysts. These are transition and late transition metal complexes with di-imine ligands, which form part of the DuPont "Versipol" technology. Such catalysts create highly branched to exceptionally linear ethylene homopolymers and linear alpha-olefins. Late transition metals offer not only the potential for the incorporation of polar comonomers, which until now has only been possible in LDPE reactors, but also their controlled sequence distribution, compared to the random composition of free radical LDPE copolymers. Such copolymers account for over 1 million tons per annum [20]. Versipol has so far only been cross-licensed and used commercially by DuPont Dow Elastomers (a former joint venture, now dissolved) in an EPDM plant.

[9]Source: US Patent Application WO 9623010.

2.7 The Progress of Polyethylene

We have seen the development of polyethylene, from low molecular weight polymers first mentioned by name in the literature in 1869, to the first reported solid polymers of linear polyethylene by Prof. Marvel in 1930; then the unintentional synthesis and chance observation of 0.4 g of solid polyethylene in March 1933 by ICI (prepared under high pressure, later described as LDPE); the onset of catalyst technology in the industry, from the simultaneous discoveries of transition metal catalysts a few decades later, that created the HDPE industry; the development of LLDPE copolymers; and the discovery in 1979 of metallocene catalysts for polyolefin polymerization – all of which are now part of the mainstream polyethylene industry. Post-metallocene catalysts offer the promise of branching without high pressure or comonomers; the potential to incorporate polar groups without high pressure, and to control this copolymer microstructure.

The three major segments of polyethylene (LDPE and its copolymers; HDPE; LLDPE) are now an industry of almost (2018E) 100 million tons with a value of $183bn [21].

At over 31 % of the global plastic market, polyethylene has indeed become "the world's leading synthetic macromolecule" [22].

The outstanding growth of this polyethylene industry over an 80-year time frame is shown clearly in Fig. 2.3, based on all data available, from different sources.

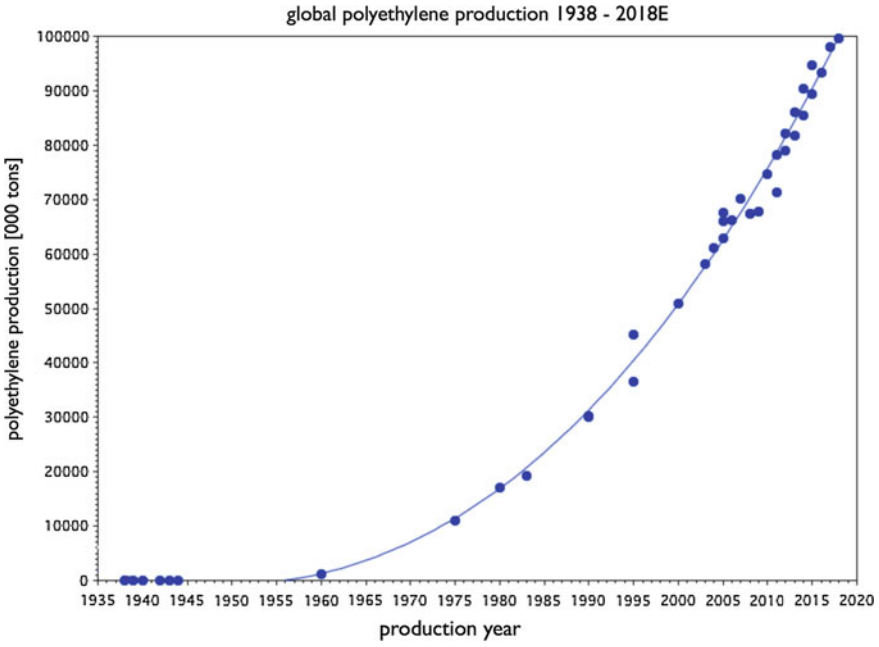
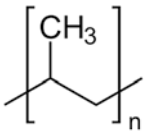


Fig. 2.3 Global polyethylene production up to 2018 (data compiled from various private and open sources)

2.8 Polypropylene (PP)

We may argue but concede that LPDE, HDPE, and LLDPE are three different kinds of polymer, albeit starting from a common monomer.



Polypropylene

This makes **polypropylene** (PP) the world's largest polymer.

Whatever our stance on this analysis, we see that polypropylene, although a comparative latecomer to the polyolefin "game", is becoming the star.

From invention in 1953 and commercialization in 1957, it has become an industry of (2018 estimate) 86 million tons (27 % of the worldwide plastic market) with a value of over $135 billion.

On the same scale as the PE growth curve just above, Fig. 2.4 shows the PP production since invention, similarly using all data available from various sources.

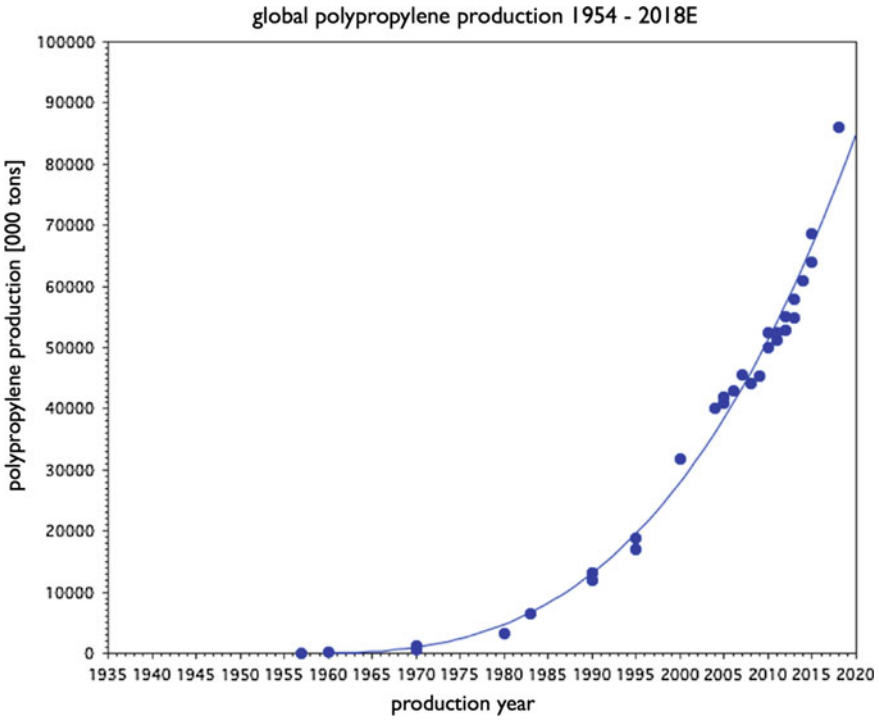


Fig. 2.4 Global polypropylene production up to 2018 (data compiled from various private and open sources)

Extrapolating, noting the faster rate of growth, we might not be surprised to find that in a decade, PP will be as big as the total PE segment.

The polypropylene story is both similar and quite different from the polyethylene story.

Let us firstly follow the strict chronology of the discoveries of crystalline polypropylene.

2.8.1 Standard Oil of Indiana

Alex Zletz noted in his laboratory journal on 18 July 1950 the suggestion that the molybdenum catalyst could be used for the polymerization of propylene. He and other colleagues carried out various experiments with propylene polymerization until July 1953, but they were not accepted as proof of priority, because later the judge ruled that "since neither the making of the product had been adequately described, nor had the product been recognized or a utility therefore been given". The economic impact of this decision is significant and provides a salutary lesson to those designing experiments, characterizing and reporting the outcomes, and making laboratory notebook entries. The judgment is based on the US law, which provides that three criteria must be met when determining prior inventorship (priority), criteria which are also internationally respected:

(1) Production of a composition of matter satisfying the limitation of the count.
(2) Recognition of the composition of matter; and
(3) Recognition of a specific practical utility for the composition.

2.8.2 Phillips Petroleum

As we saw previously, polypropylene was first made in June 1951, unintentionally as a solid polymer, by Phillips Petroleum, who were at that time seeking to convert excess refinery gases, ethylene and propylene, to high-octane fuel. Phillips developed their chromium olefin polymerization catalyst for linear polyethylene[10], but in fact, Phillips never entered the polypropylene manufacturing business. Paul Hogan and Robert Banks recorded the invention of the process by which they produced crystalline polypropylene about an hour after their discovery. As we shall see in more detail below, their January 1953 patent application was issued[11] in March 1983 (32 years after their discovery) [11].

[10]Source: US Patent 2825721.

[11]Source: US Patent 4376851.

2.8.3 Natta

Dr. Giulio Natta was a professor at the Polytechnic Institute in Milan, who worked closely with the Montecatini Company, from where he sourced most of his research staff. In 1952, at Achema in Frankfurt, he heard Karl Ziegler lecture on the polymerization of ethylene. He immediately invited Ziegler to visit Milan, at Montecatini's expense. One outcome of this visit was an agreement for the scientific exchange of information between Ziegler and Natta, which enabled three Montecatini scientists, already assigned to Natta, to work at Ziegler's Institute. There in late 1953, they learnt about the synthesis of linear polyethylene by Ziegler, and Natta asked his research group in Milan to attempt the polymerization of propylene using "Ziegler catalysts" (so entitled by Natta). Based on experiments by Paolo Chini on 11 March 1954, Natta wrote in his own notebook "today we made polypropylene". In a subsequent visit to Ziegler (May 1954), Natta asked and persisted with the question about polymerising propylene. Ziegler said he had tried it, but "es geht nichts" (it does not work). Natta was now sure that his process was "new", and he filed Italian process and polymer patents on 8 June and 27 July 1954, respectively.

2.8.4 Hoechst

Hoechst was an early Ziegler licensee for linear polyethylene. Dr. Rehn, a research chemist at Hoechst, succeeded in making polypropylene using a Ziegler catalyst in March 1954. No patent was applied for, out of respect for Dr. Ziegler's research area.

2.8.5 Ziegler

On 27 October 1953, the day after his successful PE polymerization with zirconium, Heinz Breil also investigated propylene, but concluded "propylene cannot be converted into high molecular weight polypropylene". In June 1954, Heinz Martin used new reactors to polymerize propylene to high molecular weight in good yield and demonstrated that both pure propylene and 1-butene could be easily polymerized by the new catalysts. A sixth patent was therefore submitted 3 August 1954, extending the scope to α-olefins such as propylene and 1-butene.

2.8.6 PCL

Petrochemicals Ltd., in England, were Ziegler polyethylene licensees who operated a sizeable pilot plant making polyethylene. One day in 1954, just as they were ready

to run the pilot plant, the ethylene line failed, and the technologist Bernard Wright decided to try propylene instead. It worked. Because of the understanding with Ziegler, that this was Dr Ziegler's research area, PCL – like Hoechst above – did not even consider patenting or publishing the result. Nor did they even inform Ziegler, who himself had just made polypropylene.

2.8.7 DuPont

Following the bold statement by Frank Gresham (mentioned previously), Stamatoff and Baxter conducted a series of experiments at DuPont, from April through August of 1954, using different catalysts for both ethylene and propylene. A large number of these experiments yielded either no polymer at all or liquid polymers (oils) only. In some cases, minute quantities of solid polymer were formed. On 21 May 1954, Baxter had converted propylene with the aid of a mixture of Grignard compounds and titanium tetrachloride, but the yield, 0.5 g of a powder, was not conclusive, even though a film was formed from this product, which was characterized as "tough and elastic", and infrared analysis showed that it was indeed polypropylene. No evidence of crystallinity was recorded.

Later, it was a legal judgment that they "had not only failed to recognize the polypropylene product as such, but had also neglected to show any utility, as required by the rules" and that the earliest priority established by Du Pont with respect to the production of solid, crystalline polypropylene was therefore 19 August 1954. In September 1954, DuPont learned of the work of Karl Ziegler and concluded that his work was "remarkably parallel to our own", his dates were generally earlier, and that DuPont would not dominate the Ziegler patent position. DuPont therefore paid Ziegler his customary "$50,000 to view" fee and was disappointed to find that his "process" consisted of little more than laboratory results.

2.8.8 Hercules

Hercules was one of the first Ziegler polyethylene licensees, in mid-1954. In October 1954, Edwin Vandenberg was given the assignment to do scouting work with the new Ziegler catalysts, and within a week, he had polymerized propylene with a Ziegler catalyst and had isolated an "unusual, insoluble, crystalline polymer." As we saw previously, Hercules went on to become the world's largest manufacturer of PP by the 1980s.

Catalyst research at Hercules led, in early 1955, to the development of improved catalysts. Vandenberg also discovered the use of hydrogen to control the molecular weight of polyolefins made with Ziegler–Natta type catalysts, which remains a principal method of molecular weight control today [23].

2.8.9 *"Interference"*

Between 1953 and 1956, five patent applications on the discovery of polypropylene had been filed at the US Patent Office (Table 2.1).

On 9 September 1958, the US Patent Office declared "interference" (a procedure carried out by US Patent law according to which the Board of Patent Appeals in the US Patent Office determines the priority of two or more inventions of identical or similar claim content with time overlap) between these five parties. Neither the parties nor the US Patent Office had considered including Karl Ziegler's patent rights in this proceeding.

At issue was "the priority of invention of crystalline polypropylene, a plastic with considerable commercial utility and value".

Patent Office actions and the court battle that followed lasted three decades, and produced volumes of testimony and scientific research. Indeed, the legal proceedings contained what may be the most complete scientific record of the discovery of a crystalline material. Over 1000 exhibits had been submitted and over 100 witnesses deposed in 18,000 pages of testimony by 1970. During the course of the 85-day trial conducted between 19 September 1977 and 17 May 1978, the district court received, in addition to the voluminous record compiled in the Patent Office, listed above, considerable new evidence including several thousand exhibits and the testimony of a number of experts in the area of physical and polymer chemistry.

Hercules was eliminated from the interference in 1964 by the US Patent Office because of their late discovery and patent application date. Finally (it seemed), on 29 November 1971, the board finally awarded priority of invention to the senior party, Natta et al., and US Patent No. 3,715,344 was issued to Montedison on 6 February 1973. The defeated parties then appealed the decision with a Civil Action (US District Court of the District of Delaware, Civil Action 4319). In these 1980 hearings, it was concluded that Phillips was entitled to an invention date of no later than 27 January 1953. The district court also determined that Phillips had proved that Montedison had "fraudulently withheld information from Patent Office examiners, and that this fraud was detrimental to Phillips' case for priority of invention in the Patent Office". However, because of the conclusion that Phillips is entitled to priority on the basis of its constructive reduction to practice, the issue of Montedison's fraud would have no effect on Phillips' entitlement to priority. Therefore, the court found that the crystalline polypropylene of the interference count was useful, novel, and non-obvious and therefore patentable to Phillips and

Table 2.1 PP patent filings at the US Patent Office between 1953 and 1956

Applicant	Assignee	Filing date
Natta et al.	Montedison	8 June 1954
Baxter et al.	DuPont	19 August 1954
Zletz	Standard oil	15 October 1954
Vandenberg	Hercules	7 April 1955
Hogan and banks	Philips petroleum	11 January 1956

authorized 15 March 1983 the Patent and Trademark Office to issue the patent to Phillips.[12] Phillips was able to collect $300 million in licensing revenues from polypropylene manufacturers through 1995 [24]—a considerable economic impact!

The entire story and economic impact of the ownership and licensing of polyolefin catalysts, including financial details running into millions of US dollars, have been extensively documented (297 pages) by Dr. Heinz Martin [15]. Dr. Martin mentions (p 124) that his (Max Planck) institute alone incurred expenses of more than 30 million Deutsche Marks (approximately US$ 7.5 million at the time) in the defence of its patent rights and to prosecute infringers. Even after Karl Ziegler had passed away, Dr. Martin was able to continue the patent and licensing situation in the USA, which was finally concluded after 45 years, when in 1999 a final settlement of 1.65 million US dollars was agreed with the Formosa Plastics Corp. of Texas. Among other things, they were able to compel Japanese automobile manufacturers to pay royalties for the period from 1988 to 1995, because their automobiles which were imported into the USA contained parts made of polypropylene which was produced in Japan with Ziegler catalysts!

We should perhaps note that US patent law is now internationally harmonized (since June 1995) and mandates a patent term of 20 years beginning on the date on which the application is filed, as compared to the previous "17-year term from publication, or 20 years from filing, *whichever is longer*", so such extended patent dialogues, as we have seen several examples of in this overview, with their resultant economic impact, are unlikely to be repeated.

2.9 Other Polyolefins

We have seen the development of the polyethylene industry in 80 years from 1 ton (1938) to 99.6 m tons (2018E). We saw how the original 1938 commercial polyethylene, low-density polyethylene LDPE, was complemented by the more linear, more crystalline HDPE which was discovered two decades later and then further enhanced by the reintroduction of controlled branching, through copolymerization with up to C_8 alpha-olefins, to produce still an essentially linear polymer but with short-chain branching (from the comonomer inclusion) that gave a lower density polymer, LLDPE. We will see later that this LLDPE is continuing to take share even as the total PE volume increases, approaching 1/3 of the total market of polymers made from ethylene. In parallel, we saw the development of the polypropylene sector, dominated by the Ziegler–Natta catalysis, which remains on a fast growth curve and is on track to approach the polyethylene volume within a decade.

In volume, PE and PP dominate in terms of economic impact. But they are not the entire story. We look briefly at the other polyolefins, highlighting the aspects of

[12]Phillips finally wins its patent—Chemical Week 23 March 1983.

their development that have special industrial application and economic or commercial impact.

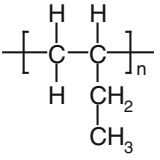
2.9.1 UHMWPE

Ultra-high molecular weight polyethylene is a linear polyethylene manufactured using a Ziegler–Natta catalyst, but with a molecular weight 10–100 times higher than conventional low-pressure polyethylene. These are very large molecules indeed: molecular weights up to 6,000,000 g/mol, a degree of polymerization of over 200,000, which means a polyethylene molecule with more than 400,000 carbon atoms in the main chain.

UHMWPE was first prepared by Karl Ziegler and commercialized as early as 1955 by Ruhrchemie AG.[13]

UHMWPE has a unique combination of properties, particularly chemical resistance, lubricity, unmatched toughness, and outstanding abrasion resistance. On account of the significant polymer entanglement due to the high molecular weight, it is not conventionally melt processible and is often fabricated by sintering (high temperature and pressure). Many industrial applications exploit the abrasion resistance of UHMWPE. A significant application, since the 1960s, when developed by Prof. (later Sir) John Charnley, has been the use of UHMWPE in hip replacements, on account of its bioinertness and outstanding abrasion resistance. This has changed the quality of life for thousands.

2.9.2 Polybutene-1



Polybutene-1, PB-1, or polybut-1-ene is another stereospecific (isotactic) polyolefin polymer, discovered by Prof. Giulio Natta in 1954. It is a linear high molecular weight crystalline thermoplastic polymer, with low density (0.91). The ethyl side groups create entanglement, which provides for the very good creep resistance of this polymer, which also has an abrasion resistance comparable to UHMWPE, and an excellent resistance to chemicals and environmental stress-cracking.

[13]Source: US Patent 3254070.

Polybutene was available as Vestolen BT since 1964 from Chemische Werke Hüls, who started the first industrial production in 1964 with a capacity of 3000 tpa. In 1973, Hüls withdrew Vestolen BT from the market after some manufacturing issues in their polymerization plant. Independently, Mobil Oil in the US developed their own PB-1 process technology and built a small industrial plant in Taft, Lousiana, in 1968. In the early 1970's, the plant was taken over and operated by Witco Chemical Corporation.

At the end of 1977, Shell acquired the PB-1 business from Witco, including the Taft plant. Shell then started a major investment programme to improve the product quality and to increase the production capacity to about 27,000 tpa. This Taft plant was closed in 2002, after 30 years of PB-1 production. A small Mitsui production capacity also existed in Japan. In 2004, a 45,000-tonne plant—the largest in the world—was opened by Basell in Moerdijk, the Netherlands, for less than $100 million, on the 50th anniversary of PB-1. This plant was debottlenecked in 2008 to reach a nameplate of 67,000 tpa. LyondellBasell Industries are now the primary supplier of PB-1 worldwide, claiming an 80 % market share, with Mitsui holding the balance.

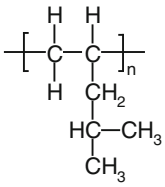
Polybutene-1 is a polyolefin with rather specialty/niche applications. A few examples are pipes for domestic and commercial hot and cold water plumbing and heating systems. Blended with PE, it forms a two-phase structure which is the basis of seal peel technology (easy-opening flexible packaging). Hot water tanks are manufactured by blow-moulding PB1.

In comparison with PE and PP, we can describe PB-1 as "a relatively unexplored polyolefin".

It remains relatively in low volume, in the scale of polyolefins that we have primarily focused on, but provides unique properties and performance, and so continues with double-digit growth.

Piping is an application example in this polyolefin industry of how legal liability has had enormous economic impact. Polybutene-1 was introduced to the European market in the 1960s, has a successful long-term record of service in pressurized hot and cold water systems, and so is widely recognized by manufacturers and installers of piping systems in Europe and Asia as the material of choice for these systems. It remains a growth area for PB1. However, polybutene piping *systems* were the subject of a large and lengthy class action legal case in the USA in the 1990s, which was actually related to the pipe connections and fittings made in acetal resin. The Polybutene Piping Systems Association (PBPSA) is focussed only on this application of PB1 and provides further detail on their Website www.pbpsa.com, where it is explained clearly that "in view of the outcome of the previous US litigation process", PB1 is not promoted (by PBPSA members) for this application in North America (in spite of historically proven intrinsic suitability).

2.9.3 TPX®



TPX® is the trade name for the polyolefin poly 4-methyl pent-1-ene.

It was originally manufactured by ICI. In 1975, Mitsui took over the entire business from ICI and the technology from BP to make the monomer. It is made solely by Mitsui today. In November 2003, Mitsui increased the annual production capacity of TPX® at Iwakuni-Ohtake Works from 68,000 tons to 75,000 tons.

A polymer of 4-methyl pent-1-ene was recorded from the earliest days (1953), as an example of the use of a transition metal catalyst to polymerize olefins.[14]

We should note that 4-methyl pent-1-ene is used as a comonomer in some grades of LLDPE.

TPX has a number of unique properties and features, but it has remained a specialty engineering polymer. It has the lowest density of any plastic material 0.835 g/cm^3. Although crystalline, it is totally transparent due to the amorphous and crystalline phases having the same density. It has very low surface energy and outstanding optical and acoustic properties. A current growth area is in films. Mitsui has a separate tradename Opulent™ for films of poly 4-methyl pent-1-ene.

2.9.4 PolyDCPD

Cyclopentadiene is a major component of the C5 stream of naphtha cracking. Because it is so reactive, it exists at ambient temperature as the stable dimer, dicyclopentadiene.

This dimer is the basis of two groups of polyolefin polymers.

The first group consists of amorphous thermoplastic engineering polymers.

These are cyclic olefin polymers (COP) or cyclic olefin copolymers (COC) with ethylene. They were commercialized, for example, as Zeonex (in 1991) and Zeonar (by Zeon), as Topas (Polyplastics), Apel (Mitsui), and Arton (JSR). Topas was originally part of Ticona, before it was sold to Daicel in 2005. A Topas plant with a capacity of 30,000 tpa started up in Oberhausen, Germany, in September 2000. Until that time, world capacity from 4 pilot-scale plants was around 10,000 tpa.

[14]Source: US Patent 4376851 Hogan.

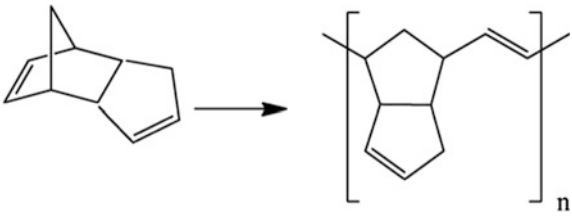


Fig. 2.5 Polymerization of DCPD into pDCPD

These cyclic olefin polymers are high-temperature (T_g up to 180 °C) polymers with good chemical resistance, outstanding optical properties, and low moisture absorption.

The early promise for COC was as a lower cost alternative to polycarbonate in optical discs, but commercialization was slow and that market has now all but disappeared.

A second group of polyolefins is made from dicyclopentadiene monomer directly, but they are thermoset polymers, processed using resin transfer moulding RTM or reaction injection moulding RIM, potentially and typically into large components in transportation (car body parts), or energy (wind turbine blades). These polyDCPD polymers are made using ring-opening metathesis polymerization (ROMP) using a Grubbs' catalyst. The process of making pDCPD is also said to be more environmentally friendly, and involving less steps, than that of making the traditional thermoset epoxy resin. Strictly speaking, they are outside the scope of this chapter, but remain a polyolefin with potential (Fig. 2.5).

2.10 The Development of the Polyolefin Industry

The economic impact of polyolefins can also be assessed by the development of the polyolefin industry—this industry is an aggregate of the companies that pioneered these materials, and the corporations that they became, or merged with. Many of the pioneering companies' names no longer exist, although new players claim their inheritance.

We have seen, as we have reviewed the development of polyethylene and polypropylene, that the commercialization, development, and manufacture of these and related polymers have involved a variety of industrial enterprises. These have been classically chemical companies (such as ICI, BASF, DuPont) diversifying into polymers; petrochemical companies moving downstream (Phillips, Standard Oil, Aramco); and other companies seeking radical diversification (W.R. Grace being an example of this, now boldly moving into polyolefin catalysts with their recent acquisition of the Unipol™ PP catalyst technology from Dow).

Over 80 years, we have seen significant activities in terms of mergers and acquisitions (M&A), asset swap, new entrants, industry consolidation, geographical

diversification, the search for lower cost bases, or low-cost or available feedstock. Other drivers have been the globalization of trade and business, the opportunity to participate in emerging and fast-growing markets, as well as the globalization of industries that are primary consumers of plastics, such as the automotive (car) industry and first tier FMCG companies such as P&G and Unilever. We see examples of the drive for product diversification and portfolio extension, often followed by a focus on core business and divestment of products that are no longer part of the perceived core business strategy.

Within the scope of this chapter, it is only possible to give some selective examples of this extensive global industrial development, not to provide an exhaustive treatment, description, and analysis.

Below, we give some descriptive examples of the development of the polyolefin industry from the perspective of individual companies, some of whom have remained in polymers but have largely exited their early polyolefin activities (such as DuPont), no longer even participate in the industry of which they were an early member (such as Hoechst AG or Monsanto, which went on to become a life science or agricultural company, respectively) or were a founding member, but no longer even exist (ICI being a prime example).

Anyone entering the polyolefin industry today, and seeing the major players of today, would be unaware of the trauma and change that this industry has seen, particularly in the last 30 years.

One way to describe the polyolefin industry today is to look at the main polyolefin producers. The (2013) Fig. 2.6 shows the top 15 polyolefin producers in the world.

By "recognizable name", only two of the early players in the polyolefin industry are listed: ExxonMobil—formerly Exxon, previously Esso, previously Standard Oil (S.O.)—at the head of the list; and Chevron Phillips, which was formed 1 July 2000 by merging the chemical operations of Phillips Petroleum Company and Chevron Corporation. Dow Chemical purchased Union Carbide Corporation for $9.3bn in 2001 and through that acquisition can claim to have been an early participant in this polyolefin industry (recalling that Union Carbide was rapidly developing ICI low-density polyethylene plants during WWII under sub-licence from DuPont).

LyondellBasell, the third largest polyolefin company in the world, has accumulated a rich heritage from the polyolefin industry through a complex history, and moreover, its formation from Basell and Lyondell in 2007 is one of the industrial deals that has made considerable economic impact. We briefly trace the Lyondell and Basell streams from the earliest days and then look at the trauma of formation, bankruptcy, and emergence as a major high-performing polyolefin producer. Figure 2.7 attempts to capture the history and ancestry and mergers related to LyondellBasell in one image.

We can start one thread in 1955, when the Texas Butadiene and Chemical Corporation bought the Lyondell Country Club in Channelview, Texas, and built a plant on that site. Sinclair Petrochemicals then purchased the Channelview site in 1962. Atlantic Refining Company and Richfield Oil Corporation formed Atlantic Richfield (ARCO) in 1966, which merged in 1969 with Sinclair, so the Channelview

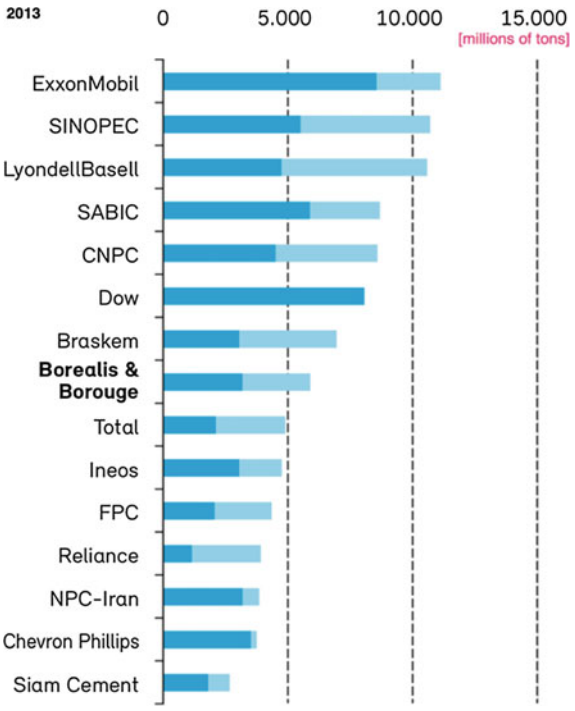


Fig. 2.6 Top 15 polyolefin producers in the world

plant then became a part of ARCO Chemical Company [25]. In 1985, Atlantic Richfield Company (ARCO) separated its olefins operations from ARCO Chemical Company, forming a new subsidiary, finally renamed Lyondell Petrochemical Company, 50 % of which was sold to the public in a $1.4 billion IPO in 1989 [26].

The next year, 1990, Lyondell purchased, from the Rexene Products Company, the low-density polyethylene and polypropylene plants built in Bayport, Texas, by El Paso Products Company in the 1970s. In 1995, the Alathon® HDPE business was acquired from Occidental Chemical Corporation for $356 million. In 1997, Lyondell combined its petrochemical and polymer businesses with those of Millennium Chemicals (which itself had recently been formed from the Quantum Chemical Company, which had been the largest producer of polyethylene in the USA) to form Equistar Chemicals as a joint venture. Occidental Chemical's petrochemical business became the third part of Equistar in 1998.

As a result of the merger, Equistar controlled $7 billion in assets with *pro forma* sales in 1997 of $6 billion. It was now North America's largest olefins producer and the second largest in the world. Lyondell acquired ARCO Chemical in 1998 for $5.6 billion, and the company changed its name to Lyondell Chemical Company. Lyondell bought the Occidental Stake in Equistar in a $400 m stock deal in 2002, and in 2004, Lyondell acquired Millennium, thus gaining 100 % ownership of Equistar.

Three tributaries flow into the Basell stream. We should perhaps start with Montecatini, to whom Natta assigned his PP patents, Montecatini merged with

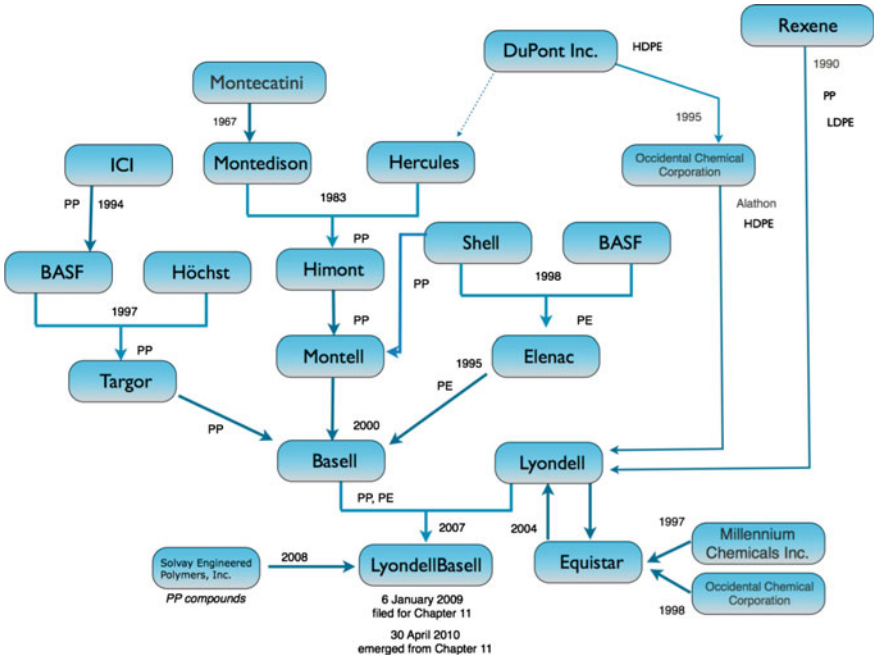


Fig. 2.7 The historical development of LyondellBasell

Edison and became Montedison in 1967. Hercules Powder Company merged their PP interests with Montedison in 1983, to form Himont, which later merged with the PP interests of Shell in 1995 to form Montell.

The second tributary is the PP thread from the early days of polypropylene at BASF, and the 1994 acquisition by BASF of the 300,000-ton PP business from ICI (who had already exited PE in 1982, when it swapped its PE business for the PVC business of BP), which acquisition doubled the size of the BASF PP business to 600,000 t. BASF merged their PP business with that of Hoechst in a venture called Targor, in 1997.

A third tributary is the polyethylene business Elenac, formed in 1998 by the merger of the polyethylene interests of BASF and Shell.

These three—Montell, Targor, and Elenac—came together as the Dutch-based company Basell in 2000. Basell was then the world's largest polypropylene maker, with 7.8 million tons of annual capacity, and the largest polyethylene producer in Europe. Basell was also a world leader in polypropylene licensing; 40 % of installed capacity worldwide used Basell technologies, such as Spheripol.

Basell lost money in two of its first three years of operation, but in 2004, generated profits of about $175 million on sales of $8.2 billion.

In late 2005, Access Industries, a privately held industrial group founded and led by Ukrainian-born, Harvard-educated financier Len Blavatnik, purchased Basell in a $5.4 billion 80 % leveraged buyout, putting down $1.1 billion in the deal. This was the largest leveraged buyout that the chemical industry had seen. Over the two

years from acquisition until December 2007, $463 million of cash was withdrawn from Basell in the form of dividends and management fees.

In 2006, Basell was the world's largest producer of polypropylene and of polyethylene, and a global leader in the development and licensing of polypropylene and polyethylene processes, and catalysts.

The next stage is what has become known as "The Lyondell Play". In July 2007, Blavatnik proposed to acquire Lyondell at $48 per share, a 45 % premium on the share price on 16 July 2007. Including the $12.2 billion to purchase these shares, a total funding of $21bn was required. Pursuant to the merger agreement, on 20 December 2007, LyondellBasell Industries (LBI), the third largest chemical company in the world, were formed by this merger of Basell and Lyondell.

In 2008, the revenue of LBI was $50.710bn with an EBITDA of $3.398bn.

It was the merger timing that was unfortunate—LBI had an enormous debt ($23.6bn), at a time when the Lehman Brothers collapse in September 2008 was precipitating a global financial crisis. Because some of the debt was asset-backed, eroding inventory values resulted in a severely diminished borrowing base and triggered LBI's obligation to repay the lenders. Lack of liquidity meant that repayments were increasingly difficult, and LyondellBasell filed for Chap. 11 bankruptcy protection on 6 January 2009.

Chapter 11 enabled a "fresh start" for LBI on many fronts, and LBI was able to exit from Chap. 11 on 30 April 2010 with a "favourable capital structure".

LBI was also well placed to benefit from the emergence of low-cost shale gas (ethane) at that time, to feed the six crackers it had in the USA. They were converted for minimal capital investment, to be able to run 90 % of the time on ethane.

Quickly recognizing and taking advantage of this new feedstock opportunity significantly improved margins and profitability, such that other investors are challenging companies like Dow, asking why they are not performing as well as LBI.

LyondellBasell was listed on the New York Stock Exchange starting 14 October 2010, opening around $27. In September 2014, a peak of $115.40 was achieved.

Figure 2.7 shows the polyolefin thread of the historical development of LyondellBasell.

2.10.1 The Development of the Polyolefin Industry in the Gulf Cooperation Council (GCC)

We have looked in some detail at how the polyolefin industry has developed from those who originated it. We now turn to the GCC region, which has developed a polyolefin industry from nothing in the last 20 or 30 years. There is a major polyolefin industry in Saudi Arabia, but within the constraints of this chapter, we have selected two examples, and for each, we illustrate the progress and status through a chart similar to the one we prepared for LyondellBasell Industries. The first is Qatar, the first GCC country to have a polyolefin industry. The second is the

UAE, where the sovereign wealth fund has acted strategically and boldly, and has created a polyolefin group with global and regional impact.

2.10.2 Qatar

The State of Qatar was the first GCC state to have a polyolefin industry. The first production of polyolefin in the GCC was an LDPE plant inaugurated by QAPCO in 1981. In Fig. 2.8, we attempt to show in one image the historical development and ownership of this polyethylene industry. The strong French partnership is evident. The outcome, after 35 years, is the emergence of a major plant for each major kind of polyethylene.

2.10.3 The United Arab Emirates (UAE)

The International Petroleum Investment Company (IPIC) is the long-term strategic investment arm of the government of Abu Dhabi, established by the visionary Sheikh Zayed 30 years ago. In the last 20 years, IPIC has purchased, developed,

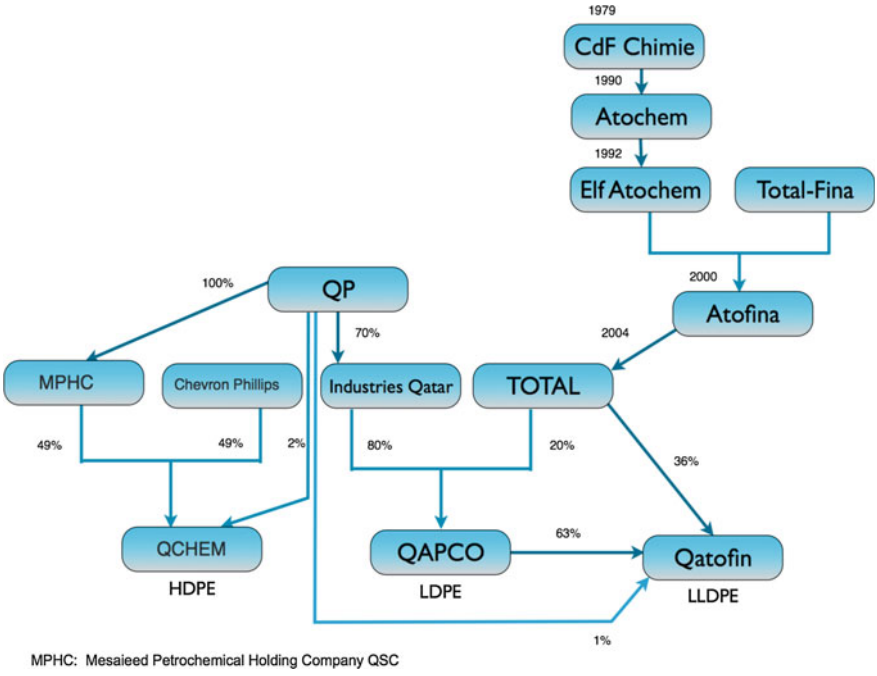


Fig. 2.8 Development of the polyolefin industry in the State of Qatar

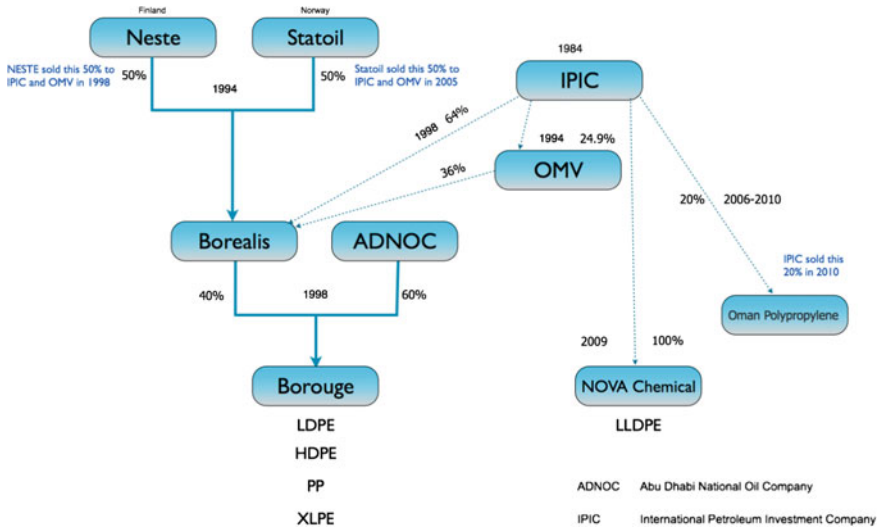


Fig. 2.9 Development of the polyolefin industry in the UAE

and nurtured a portfolio of companies in the polyolefin industry. Today, the IPC portfolio consists of Nova Chemicals, Borealis, and Borouge. Little effort seems to have been made in the 5 years since acquiring Nova to integrate it within the Borealis/Borouge sphere, or develop any synergy between these three companies (Fig. 2.9).

2.11 Industrial Economic Impact

We have seen how the economic impact of polyolefins can be assessed by the development of the polyolefin industry, in terms of company development and merger and acquisition activity. Numerous M&A transactions have cumulatively resulted—from the time perspective of decades—a radical transformation and reshaping of the industry.

One characteristic of the polyolefin industry is that it is capital-intensive. This is a dimension of economic impact—the amount of money to be invested to create this industry. Unlike the downstream polymer processing and converting industry (where the classical start-up might be imagined as one small moulding machine in a garage), even the smallest polyolefin manufacturing process (the Hüls PB-1 plant at start-up was just 3000 tons per annum) involves capital investment in the order of millions of dollars.

World-scale plants today for PE and PP are very much bigger than when the industry started, of course, by more than three orders of magnitude. Recall that the earliest ICI LDPE plants were 100 tons per annum! The first 1957 polypropylene

plant was 6000 tons per annum. By 1965, typical new polyolefin plant capacities were 10,000 tons per annum; in the early 1970s, around 25,000 tons per annum, and by 1985, we were at 80,000 tons. By 1990, 100,000 tons per annum was the norm, increasing to 300,000 tons by 2000. The newest plants being built now are more than 450,000 and up to 750,000 tons per annum.

Despite these changes in production capacity, the *basic* process for making polyolefins has really changed little since 1960 [27]. What has happened is that the cost per unit of output has been reduced through the massive increase in the scale of the plant. In addition, improvements in process, process control and automation, process equipment, and catalyst technology have all contributed to lower polymer conversion cost, and improved and more consistent product quality.

In spite of significant capital investment (we now need to think in the investment range of $500–1000 million per world-scale state-of-the-art plant), these highly automated plants provide only minimal employment opportunities. They offer interesting, challenging, demanding, and well-paid positions, but relatively few of them, and only for appropriately qualified and experienced professionals. The polymers, if converted locally, provide many further opportunities for employment, so that the plant and its downstream value chains make a significant contribution to the local economy, whether through local consumption or for export.

How many of these polyolefin production plants have been installed since the beginning of this industry? One way to develop the answer to this question, which we do not pursue in depth here, is to follow the technology licensors. For example, we know that ICI were active in licensing LDPE and that by 1977, they had 23 licensees, and a total installed capacity of 812,000 tons. However, their founding technology was based on the stirred tank reactor (autoclave), and this could not be scaled up in the same way that tubular reactors, developed by others, could. By 1980, ICI had lost the "first producer advantage", had not led the way in technology development, and in 1982, exited the PE business.

It is estimated (GEM-CHEM) that there are 170 polypropylene sites and 376 polyethylene plants, worldwide. We have seen above that the additional polyolefins (polybutene-1, TPX, pDCPD) are made in only a handful of plants around the world, so it is likely that there are over 500 plant sites around the world producing polyolefins.

2.12 Globalization, Feedstocks, and Feedstock Availability

The synthetic polymer industry started in 1910 when the thermoset moulding resin Bakelite® was commercialized and has become a global industry in the intervening 100+ years. The synthetic thermoplastic polymer industry started in Europe and developed in Europe and the Americas and Japan. Then, there was a shift of production and consumption to Asia-Pacific, particularly China, and a shift in production to the Middle East, in the last 30 years. The polyolefin industry has perhaps even led this shift. Five of the major polyolefin producers (in the list of the

top 15, we saw previously) are from Asia-Pacific, and three of them are based in the Middle East. That is a radical reshaping of the industry. This globalization is an irreversible process.

The shift to Asia is now supported by local regional demand, not just driven by the availability and low cost of labour, so we do not expect to see anything but an increasing demand from this region, as the per capita income increases, the middle class develops, and consumer expectations increase in these populous nations. China became the world's largest market for polymers as far back as 2002 and as of 2013 has a share of 30 %, compared with just 6 % back in 1983. The rest of Asia-Pacific accounts for another 15 %.

However, the shift of production to the Middle East was driven almost entirely by the availability of abundant and low-cost feedstock and investment capital, supplemented to a small extent by low-cost energy, but not by regional demand. The Middle East industries are still primarily export driven. Now that hydrocarbon feedstocks are less available in the Middle East, the capital will in future seek out alternative feedstocks based on cost and availability.

We see two feedstock factors already at play. First, we saw how the availability of low-cost ethane (shale gas) dramatically improved the economic performance of LBI after emerging from Chap. 11. We did not so far discuss Ineos, but they were, at a similar time, also heading for financial difficulties, after their $9bn acquisition of Innovene, which immediately resulted in a downgrading of their credit rating because of the leverage. Shale gas was also their saviour. It is clear that the availability and low cost (not as low cost as the Middle East, but 1/3 or 1/4 of what it was in North America not so long ago) of feedstock are drawing investment and have led to some moth-balled crackers being returned to operation. That story has only just begun and may soon build a momentum and investment direction for the next decade.

The second feedstock factor is the use of coal in China. The quantity is vast and the cost is low, both of these positive factors being offset by logistics (it is stranded coal) and concern about the quality of both the feedstock and the impact of the low quality on the environment. Oil has been the feedstock of choice for most of the world since WWII or earlier, except for a few countries, notably South Africa where political factors forced the development of an entire chemical industry based on coal. It has been remarkable to see the development of a chemical industry in China based on coal in perhaps just 10 or 15 years. "Coal to olefins" (CTO) is a reality there. Synthesis gas is produced from coal and then used to make methanol, which is then converted to olefins (ethylene or propylene). Coal to olefins is happening fast in China, it is happening widely (over three dozen projects are described), and it is likely to be as significant or more significant than the North American shale gas phenomenon.

Both of these trends— shale gas and coal to olefins—will likely be impacted by the recent (2014) drop in oil price from over $100/barrel, down to (almost) $45/barrel. Such very low oil prices make shale oil, shale gas, and deep sea drilling less attractive or even uneconomic.

Other feedstocks are there. Some polyethylene is made now in Brazil from ethylene made from ethanol from sugar cane. That is marketed and touted as though

it is a revolutionary step forward. In fact, it is just returning to the roots, but perhaps that is unknown to many. The very first polyethylene made at ICI in 1933 was made from ethylene that was made by dehydrating ethanol produced by the fermentation of molasses. The tar sands continue to be an alternative hydrocarbon source, even if it is not daily in the headlines. Almost no one is looking at the 20 gigatons of methane hydrate in the oceans or tundra.

Although it is said (for example in Saudi Arabia) that there is no natural gas available anymore, that is, at best, an inaccuracy. The fact is about 3/4 of the natural gas available in Saudi Arabia is burnt in power stations, rather than turned into valuable petrochemical feedstocks and specialty materials. The industry needs the critical feedstock for growth, and if the feedstock is not available in adequate quantities, investors will take that industry to an available feedstock source.

2.13 The Future of the Polyolefin Industry

From the materials point of view, we have clearly seen that both the total polyethylene and the polypropylene industries are still on an ascending curve, far away it seems from a plateau in terms of growth. This is clear from production forecast data in Figs. 2.2 and 2.3 discussed earlier in this chapter.

Indeed, it seems that PP, even as the latecomer, may be developing more rapidly, and we suggested that in perhaps another decade, we might see both industries of a similar size.

By then, we will have a polyolefin industry of over 200 million tons and a value above $250 billion.

The profile of the polyethylene industry itself is likely to change, in line with trends that are well developed. LLDPE continues to take share, whilst LDPE still

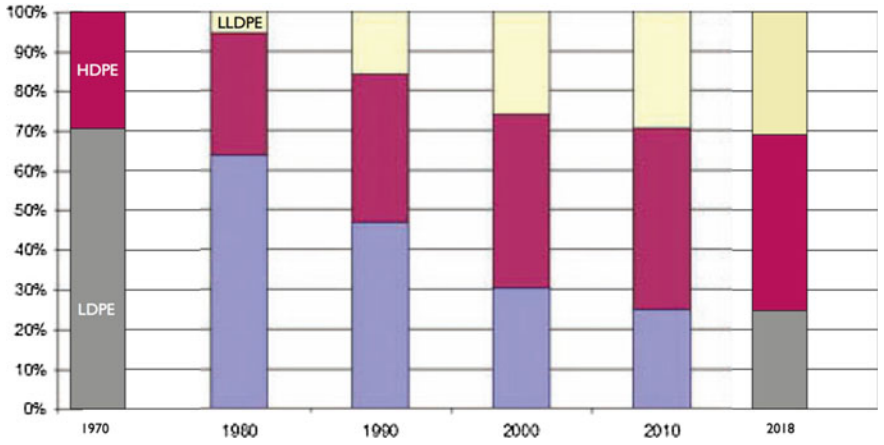


Fig. 2.10 Evolution of the polyethylene industry by PE type up to 2018

continues to grow absolutely albeit slowly from a large base. The evolution of the polyethylene industry from 1970 with an estimate forward to 2018 is shown in Fig. 2.10.

We expect that by the end of this decade, LLDPE may comprise fully 1/3 of the PE industry.

2.14 Concluding Remarks

We have considered the historical development of polyolefin polymers, looking in some detail at those who were at the forefront of this industry—some by purpose and intent, quite a number by serendipity and chance. We have explored some examples of how companies and countries have developed their polyolefin position and heritage.

We noted that the polyolefin industry developed at the same time and in parallel with the scientific recognition of polymers as giant molecules. We identified early on what have become important drivers to this day for the growth of the polymer and polyolefin industry—such themes as materials substitution; such activities as product and application development, achieved through understanding customer needs as well as the properties, processing and economics of the polymers.

We touched on various aspects of intellectual property such as patents and licensing, and how they determined the development and more importantly ownership of the new technologies.

Globalization and changes in geographical and regional importance were identified. Feedstocks—changes in the variety, the availability, and the economics—were found to be remain a fundamental driver for the polyolefin industry, and we noted that we are at several critical junctures on this topic, as we write.

The polyolefin industry is capital-intensive, for building plants, developing and upgrading them, and for investment in research, technology, and innovation for a competitive future. This industry itself provides promising and challenging careers and employment opportunities, and the associated downstream value chain—polymer conversion and processing—provides additional and more numerous employment opportunities.

Polyolefins have had a great economic and global impact as was demonstrated in this chapter. They continue on a strong growth curve, and we expect that they will have even a greater impact in the future. We concur with this statement:

> Polyolefins are indispensable in our daily lives (Borealis 2014)

We trust that you have seen and observed that polyolefin polymers are indeed now ubiquitous and indispensable in every aspect of our lives, and we hope that you have enjoyed this unique and unusual journey with us, as we have illustrated the development and economic impact of this vast polyolefin industry from its inception about 80 years ago, as much as we have been enriched as we have developed it for you.

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