

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

History of Polyolefins

H. R. Sailors^a; J. P. Hogan^a

^a Research and Development Phillips Petroleum Company, Bartlesville, Oklahoma

To cite this Article Sailors, H. R. and Hogan, J. P.(1981) 'History of Polyolefins', Journal of Macromolecular Science, Part A, 15: 7, 1377 – 1402

To link to this Article: DOI: 10.1080/00222338108056789

URL: <http://dx.doi.org/10.1080/00222338108056789>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

History of Polyolefins

H. R. SAILORS and J. P. HOGAN

Research and Development
Phillips Petroleum Company
Bartlesville, Oklahoma 74004

ABSTRACT

The history of polyolefins actually began in the 1890s with the synthesis of polymethylene from diazomethane. In the 1930s researchers in England discovered that ethylene at high pressure and in the presence of oxygen polymerized to a high molecular weight resin. Further research there and in the United States at still higher pressures yielded essentially straight chain, higher density polyethylenes. Early in the 1950s, groups in the United States and Europe independently discovered that linear, high-density polyethylenes could be made at low pressure over heterogeneous catalysts. Concurrently, groups catalytically produced polyolefin plastics from propylene and higher α -olefins. The inventorship of crystalline polypropylene was awarded to Phillips Petroleum Co. by United States courts in early 1980 (subject to final appeal). Commercial production of low-density polyethylene began in England (ICI) in 1939. High-pressure plants appeared in the United States (Du Pont and Union Carbide) and in Germany during World War II. Production of linear polyethylene started in late 1956 in the United States (Phillips). A semiworks Koppers plant began polyethylene production for commercial use earlier in 1956. Other plants quickly followed suit, using Phillips and Ziegler processes. Polypropylene production began in Europe and in the United States in 1957-1958. Two other polyolefin plastics have been produced in small commercial quantities, starting about 1965: poly(4-methyl-1-pentene) and poly-1-butene.

INTRODUCTION

The history of polyolefins is of particular interest because it encompasses the largest volume synthetic resin (polyethylene) manufactured today. As a basis for delineating the scope of resins to be considered in this history of polyolefins, composition and structure have been chosen as the controlling features. The term "polyolefin" implies the polymerization of olefins to high polymers, but to base the subject matter on this alone would leave out a historically important resin—polymethylene. This basis is not new and has previously been employed, e.g., by Raff [1] and by Bawn and Ledwith [2]. Empirically, polyethylene has been represented as $(-\text{CH}_2-)_x$ and $(-\text{C}_2\text{H}_4-)_x$, end groups being neglected in each case. One can postulate that the first formula fits polyethylene only if x is an even integer, but from the practical standpoint, a perfectly linear ethylene polymer could not be distinguished from a perfectly linear methylene polymer simply on this basis. Consequently, the terms "polyethylene" and "polymethylene" are used here as a matter of convenience to differentiate between methods of synthesis without implying that they are two separate products.

POLYMETHYLENE

In the period of 1897 through 1938, production of polymethylene by diazomethane decomposition appeared in the literature numerous times. Such publications were by Hinderman [3], von Pechman [4], and Bamberger and Tschirner [5] in 1897-1900; by Hertzog and Schonbach [6] in 1912; by Meerwein and Burneleit [7] in 1928, and by Werle [8], a student of Meerwein's, in 1938. Catalysts such as unglazed china, amorphous boron, and boric acid esters were used. From work on the products, the melting points were found to be 126.5 and 128°C and the empirical formula to be CH_2 by carbon-hydrogen analysis. The product was called polymethylene and the formula expressed as $(-\text{CH}_2-)_x$. Analysis showed the polymer to be free of nitrogen. Solubility in common organic solvents was reported as very slight.

The data reported in these publications were not as complete as more recently desired on high polymers, and Phillips Petroleum Co. repeated the work of Werle [8] and Bamberger and Tschirner [5]. Results [9] of analysis and testing were: carbon, 85.5-85.8 wt%; hydrogen, 14.3-14.7 wt% (calculation for CH_2 is 85.6 wt% C and 14.4 wt% H); crystallinity (x-ray), 90-92%; side chains, ≤ 0.4 per 200 carbons; 134-137°C melting point; 3720-4140 psi tensile strength; 1.13-1.22 relative viscosity (0.125 wt% polymer in xylene at 85°C); 0.964-0.970 g/cc annealed density. Very similar data were obtained by Hoberg and Ziegler [10].

In 1938 and 1940 Pichler [11] and Pichler and Buffleb [12] published work on separation (by sequential extraction with boiling solvents) of hydrocarbons produced by hydrogenation of carbon monoxide over ruthenium and cobalt catalysts. The ruthenium catalyzed (1000 atm) product was extracted with a series of five hydrocarbon solvents (pentane through octane). A saturated fraction of 12 to 15% of the original product was isolated which had a melting point of 132-134°C, a density of 0.980 g/cc, and a number-average molecular weight of 23,000 (weight-average molecular weight would be significantly higher).

Raff and Lyle [13] stated that the high-density polymer was discovered before low-density polyethylene, and they refer to Hoberg and Ziegler's publication [10] in which those authors recognized that the Ziegler product and the polymethylenes of Meerwein and Burneleit [7] and Werle [8] were the same.

DISCOVERY OF POLYETHYLENE- HIGH-PRESSURE PROCESSES

As related by Swallow [14], Imperial Chemical Industries (ICI) started a high-pressure research program in 1932. In 1933, a mixture of ethylene and benzaldehyde at 170°C and 1400 atm produced a reaction which coated the walls of the reactor with a thin layer of a white waxy solid, recognized at the time as being a polymer of ethylene. On repeating the experiment with ethylene alone, a violent reaction occurred which caused rupturing of the apparatus and produced hydrogen, methane, and amorphous carbon. With more suitable apparatus available in 1935, ethylene was polymerized at high pressure and at 180°C, with 8 g of polyethylene being recovered. After much work it was found that following a leak, the ethylene used in repressuring happened to have the right amount of oxygen to cause the polymerization to take place.

The polyethylene produced at this time had a melting point of about 115°C, density of 0.91-0.92, could be drawn into filaments, and exhibited "cold drawing." Based on earlier observations by Carothers, these properties were believed to indicate polyethylene to be a reasonably straight-chain, high molecular weight polymer. As indicated by Swallow [14], polyethylene had been considered up to 1940 as a purely linear long-chain hydrocarbon, with the partially crystalline nature noted by Bunn [15] fitting well with the fringed micelle theory to explain the morphology of the polymers.

In an ICI British patent [16] based on three provisional applications filed in 1936, there were disclosed pressures of 500 to 3000 atm, temperatures of 100 to 300°C, the necessity of removing heat to control temperature, and the necessity of controlling the oxygen content of the ethylene used. Molecular weights (Staudinger) of 2,000 to 24,000 were said to have been obtained. In these applications the product was described as both $(-\text{CH}_2-)_x$ and $(-\text{C}_2\text{H}_4-)_x$.

POLYETHYLENE STRUCTURE STUDIES

In 1940 Fox and Martin [17] found by infrared that there were more methyl groups in high-pressure polyethylene than could be accounted for by the end groups. From then on, the presence of chain branching in the molecule was recognized, and the resulting studies of branching led to better understanding of mechanical properties, morphology, and the effect of synthesis conditions. The understanding of polyethylene gained in the 1940s was the result of many workers' efforts.

In 1950 and 1952 Buckley, Cross, and Ray [18] and Buckley and Ray [19] prepared polymethylene from diazomethane and additionally introduced methyl and higher branches by including controlled amounts of diazoethane or higher alkyl-substituted diazomethane compounds. For polymethylene they found a melting point of 132°C and d_4^{20} of 0.965, higher than the then-known low-density polyethylene. They further found that with the introduction of methyl branching, polyethylene-like polymers of lower density were produced. Rubbery polymers were produced when, e.g., 15 or more methyl branches were introduced for each 100 carbon atoms. This, along with other investigations too voluminous to review, provided a much improved understanding of the role of branching in polyethylene and its effect on crystallinity and other properties.

DEVELOPMENT OF HIGH-DENSITY
ETHYLENE POLYMERS

In this same general period the operating range of pressure for ethylene polymerization was extended above the 3000 atm of the original British patent, Kruse [20] showing an upper pressure of 4000 atm and Larcher and Pease [21] disclosing 5,000 to 20,000 atm, each patent showing free radical initiators. Larcher and Pease disclosed that their pressure range produced polyethylene with densities of 0.95-0.97 g/cc, tensile strengths between 2,900 and 11,800 psi, relative viscosities of 1.0 to 1.5 (0.125% in xylene at 85°C), branching to the extent of less than one side chain per 200 carbon atoms, and melting points above 127°C. The Larcher and Pease patent has claims to polyethylene including the above properties.

Low-pressure processes for high-density polyethylene were discovered in the early 1950s. Patent applications were filed by Zletz [22] in 1951, by Hogan and Banks [23] in early 1953, and by Ziegler, Breil, Martin, and Holzkamp [24] in late 1953. The term "low-pressure" is to be taken relative to the pressures of the high-pressure, free radical processes. Operating pressures of 100-200 psig up to about 1500 psig are usually employed, although more or less pressure can be used. All of these processes are catalytic.

The Zletz (Standard Oil of Indiana) patent [22] describes a supported reduced molybdenum oxide or cobalt molybdate catalyst on

alumina, with the ethylene preferably contacting the catalyst in an aromatic solvent to effect the polymerization. The patent examples show operating temperatures from 100 to 270°C. Depending on conditions, products vary from greases to high molecular weight, tough resins.

Hogan and Banks (Phillips Petroleum Co.) patents [23] describe the starting catalyst as being hexavalent chromium oxide on silica, alumina, or silica-alumina, activation usually being with air or other oxygen-containing gas at elevated temperature. The process was primarily conducted as a liquid-phase operation employing paraffins or cycloparaffins as preferred reaction media. Preferred reaction temperatures are in the range of about 60 to about 190°C. Polymer characteristics, particularly molecular weight, can be varied by changes in the activation and operating conditions.

The process of Ziegler and co-workers described in the German patent [24] employs an organometal catalyst using an aluminum tri-alkyl with a transition metal compound of Groups IVa through VIa (Ti preferred), temperature of at least 50°C, and pressure of at least 10 atm. The later U.S. patent [24] indicates aromatic, paraffin, and cycloparaffin reaction media to be suitable.

Each of the catalytic processes summarized above in terms of the initial patents has been the subject of much further research and development. It is beyond the scope of this discussion to get into the literally thousands of patents and publications describing this subsequent widespread work. Table 1 provides information on the early work for these three processes.

As of today, polyethylenes of densities from about 0.90 to about 0.98 g/cc have been produced. The differences are mainly those caused by variation of branching, though molecular weight enters importantly into the picture. Polyethylenes branched from five or six methyl groups per 100 carbon atoms to essentially unbranched polymers have been produced as commercial products. With decreased branching, the polymer increases in melting point, density, stiffness, tensile strength, crystallinity, and modulus of elasticity, thus providing a wide choice of properties to the users.

CRYSTALLINE POLYPROPYLENE— A NEW COMPOSITION

In the case of crystalline polypropylene, the polymer itself has been a commercial product for many years, but the question of who first invented the product has been the subject of intense argument in the U.S. Patent and Trademark Office and the Federal District Court (Delaware) for more than 20 years. Although scientific publications and available patents provide a considerable amount of information on the discovery of polypropylene, the Patent Office and court records provide a bonanza of additional scientific and historic information unavailable elsewhere.

TABLE 1. Early Dates of First Low-Pressure Polyethylenes

Process	Approximate date of first laboratory development	Filing date of first patent application	Polymer density (g/cc)
Standard (Indiana)	Last half 1950 [26]	April 28, 1951	0.96 [26]
Phillips	Last half 1951	January 27, 1953	0.95-0.97
Ziegler	November, 1953 [27]	November 17, 1953	0.94 [14, 28] ^a

^a Later developments provided densities to 0.965.

The Patent Office declared an interference [29] in 1958 involving five patent applications. (An interference is a proceeding in which evidence is presented to the Patent Office from which a decision is reached as to whom it believes first invented the subject matter and is entitled to a patent thereon.) The subject matter, or "count," of the interference was as follows:

Normally solid polypropylene, consisting essentially of recurring propylene units, having a substantial crystalline polypropylene content.

The interference was declared with the following five parties: E. H. Vandenberg (Hercules, Inc.); J. P. Hogan and R. L. Banks (Phillips Petroleum); A. Zletz (Standard Oil Co., Indiana); W. N. Baxter, N. G. Merkle, I. M. Robinson, and G. S. Stamatoff (DuPont); and G. Natta, P. Pino, and G. Mazzanti (Montecatini, now Montedison S.P.A.). Vandenberg was dropped from the activities because he could not show sufficiently early dates for his work.

The catalysts used by DuPont and Montecatini were organometallic. The catalysts used by Standard and by Phillips were supported metal oxides as described for polyethylene.

As background for what follows, it should be understood that two bases for a completed invention exist in patent law; these are termed an actual reduction to practice and a constructive reduction to practice. In an actual reduction to practice of a polymer (here polypropylene), the inventor must make the product of the count, recognize the polymer, and recognize a specific practical use for the polymer, each of these being provable. A constructive reduction to practice consists of filing a patent application telling how to make the polymer, adequately describing that polymer, and giving a practical use for it. Such a patent application must meet all other requirements of the Patent Office.

In the Patent Office, the Montecatini applicants were judged to be the first inventors [29], and U.S. Patent 3,715,344 was issued to them on February 6, 1973.

The Patent Office decision was appealed to the Federal District Court (Delaware) by each of the three losing parties in 1972, these appeals being consolidated into a civil action in 1975 [26]. After a trial lasting 7 months, beginning September 19, 1977, and generating about 15,000 pages of testimony and hundreds upon hundreds of exhibits, the Court reversed the Patent Office decision and concluded (January 11, 1980) that the Phillips applicants, Hogan and Banks, were the first inventors of crystalline polypropylene. The Court concluded that Phillips had proven making the crystalline polypropylene four times in the period of October 9, 1951, to April 16, 1952, and had met the other requirement for actual reduction to practice. Additionally, the Court concluded that the Phillips U.S. patent application filed

January 27, 1953 [23] was a constructive reduction to practice, meeting all the necessary legal requirements.

The Montecatini applicants made crystalline polypropylene in Italy in the period between March and June 1954 [30, 31], but they were limited in the interference to the date of the first filed Italian patent application [31], June 8, 1954. Any date in this range is about 2 years later than the dates of Hogan and Banks.

The DuPont claims to making crystalline polypropylene on May 17, 1954 [26], and to filing an adequate patent application [32] on August 19, 1954, were upheld by the Court. However, the Court said DuPont failed to satisfy the product recognition and showing of utility requirements of an actual reduction to practice. Thus, while DuPont did make crystalline polypropylene by May 17, 1954, for patent purposes they were limited to the date of filing of the patent application, again about 2 years later than the Hogan and Banks' dates.

Standard conducted work on propylene polymerization in the last half of 1950 and in late April through about July 1953, two products being made in the latter period [26]. A patent application was filed on October 15, 1954 [33]. The Court agreed with the opposing witnesses that the 1950 products were not the polypropylene of the count but were copolymers. Concerning the products of the 1953 period, the Court agreed with Standard that those two products were the crystalline product of the count and that one was recognized as being that product. The Court said the actual laboratory work failed to show that these later polymers had a practical use, and Standard was awarded the date of the filing of the patent application, October 15, 1954, as the best date for the interference.

The decision handed down by the Court, which is 200 typewritten pages, contains a large amount of information on each party's work, but in more condensed form than in the massive transcript of the court proceedings. The Court's decision can be appealed to a higher court by any or all of the losers (in appeal, December 1980). In summary of the Court's findings, the Phillips inventors were first actually to make crystalline polypropylene, the Standard inventors were second, and the DuPont and Montecatini inventors almost a tie for third and fourth places. But as decided by the Court on legal grounds, the order was Phillips first, Montecatini second, DuPont third, and Standard fourth. These initial separate successes were apparently completely independent, each without any knowledge of the others' work, and all taking place in a period of 3 years.

HIGHER 1-OLEFIN POLYMERS

By mid-1952, Hogan, Banks, and co-workers had produced polymers of 1-butene, 1-pentene, 1-hexene, and 4-methyl-1-pentene. They had fractionated the products and by infrared analysis shown the structure of each of these polymers as well as polypropylene to be

head-to-tail [34a]. In particular, the poly-4-methyl-1-pentene was described as a tough, solid polymer with a melting point in the range of 210°C (410-420°F) [34b]. These polymers were produced with supported chromium oxide catalysts [23].

In the period between March 1954 and late July 1954, Natta and co-workers produced polymers of 1-butene and 1-hexene in addition to polypropylene [30, 31]. In one of the patent applications it was stated that polymers from α -olefins higher than 1-butene were more interesting as elastomers. In a (June 8, 1955) U.S. patent application [35], poly-1-pentene had been added, with first-order transitions given for all but poly-1-hexene, which was indicated to be amorphous at 20°C. In late 1955 and 1956, Natta and co-workers announced [36-38] their syntheses and descriptions of polymers of branched chain α -olefins including 3-methyl-1-butene, 4-methyl-1-pentene, 5-methyl-1-hexene, and 5-methyl-1-hexene.

From a patent to Haven filed June 23, 1955 [39], it is evident that DuPont also soon followed its polypropylene work with polymerization of higher 1-olefins. Examples in this patent include high polymers made from 3-methyl-1-butene, 4-methyl-1-pentene, 4,4-dimethyl-1-pentene, 4-methyl-1-hexene, 4,4-dimethyl-1-hexene, 3-cyclopentyl-1-propene, and 3-cyclohexyl-1-propene. A polymer of 4-methyl-1-hexene is shown with a crystalline melting point of 160°C, all others being from 225 to over 350°C, the temperature limit of the melting point apparatus used.

STRUCTURE-CRYSTALLINITY RELATIONSHIPS

The structural studies spawned by the discovery of crystalline polymers of propylene and higher α -olefins discussed above led to the findings that the crystallinity was related to the steric regularity of the alkyl branches on the alternate carbons along the main chain of the head-to-tail polymers. For an accurate historical perspective of the discovery and structural studies of these crystalline polymers, it is necessary that the earlier contributions of other scientists be considered.

In 1943, Alfrey, Bartovics, and Mark [40] proposed that different amounts of branching along the polymer chains of several polystyrenes were responsible for the differences in properties. But in 1944, Huggins [41] proposed an explanation of these differences based on steric regularity of the phenyl side groups along the chain, saying,

In a polymer produced at low temperature one would expect a tendency toward some regular sequence of disposition of H and R, such as one in which all the R groups would be on the same side of the plane of the zig-zag carbon chain if the molecule were stretched out, or one in which the R groups alternated from one side to the other. In a polymer produced at a high temperature, a more random sequence would be expected. (Emphasis in original.)

Huggins extended the explanation to other high polymers of the general formula $(-\text{CH}_2\text{CHR}-)_x$, noting that randomness of H and R dispositions was probably responsible for the poor crystallinity of stretched polymers of this general formula.

Though not working with α -olefins, Schildknecht and co-workers [42] were probably first (1949) to make rubbery and nonrubbery vinyl high polymers (vinyl butyl ether polymers), to show a difference between the two through the use of x-ray, and to correctly attribute this difference to the placement of the side groups. They also recognized that the main chain might not be zig-zag but determined by the d and l placements of the side groups, such placements possibly being all on one side, alternating, or completely random. Crystallinity of the nonrubbery polymers was attributed to regularity of the side chains. Natta, Bassi, and Corradini [43] a few years later confirmed this, making poly(vinyl isobutyl ether) by the same method and finding complete structural analogy between this polymer and isotactic poly(5-methyl-1-hexene).

After Natta and co-workers had made polypropylene in 1954, followed closely by other poly-1-olefins, they studied intensively the structure and morphology of these polymers and published prolifically on their findings in the period 1954-1960 [44]. They found the polymers to be head-to-tail in chemical structure and, with the exception of poly(1-hexene), to have partially crystalline fractions separable by solvent extraction, melting points for fractions being determined. Principally by x-ray study of the crystalline fractions, it was established that the crystallinity of the polymers resulted from a steric structure of long sequences, with all of the alkyl groups lying on one side where the main chain was rolled out in a plane as described by Huggins [41]. They further established that in the polymer crystals the chains had a spiral conformation with alternating right- and left-hand spirals in adjacent chains. They also found that in a relatively small number of polymers they could identify sequences in which the alkyl groups lay alternately on opposite sides of the plane. Natta termed those sequences with alkyl groups on one side of the plane to be isotactic, those alternating to opposite sides of the plane to be syndiotactic, and those with random positions to be atactic. This terminology is well accepted at this time.

As is true of any major field, continuing work by a large number of scientists has greatly amplified the information initially available on poly-1-olefin structure and morphology, including additional crystal forms and further details of chain conformations throughout the partially crystalline polymer mass.

While the history of polyolefins so far has been discussed with respect to homopolymers, olefin copolymers were also made by the catalytic processes and by mixed diazo compounds. Using small amounts of comonomer along with the principal monomer, polymers of modified physical properties were made. Tailoring of products was possible to fit specific uses a bit better than homopolymers.

(Major property changes were also found possible, such as making ethylene-propylene copolymers with properties similar to rubber.)

COMMERCIAL PRODUCTION OF POLYOLEFINS

Polyethylene-High-Pressure Processes

The first plastic polymer from olefins to be discovered and the first to be produced commercially was polyethylene. ICI started up a small plant in England in September of 1939. The plant had apparently been sized to meet the estimated requirements for coating telephone and telegraph cable to be laid on the ocean floor. The polymer appeared to have properties which were ideal for this application: high dielectric constant, low dielectric loss at high frequencies, high moisture resistance, and excellent flexibility and toughness [14].

The ethylene monomer used for this new venture at first had to be made by the catalytic dehydration of ethyl alcohol [14]. This was a sobering situation. However, in a few years, all ethylene monomer was being made by the thermal cracking of petroleum fractions ranging from ethane to gas oil.

The start of World War II quickly changed both the use and the demand for polyethylene. Polyethylene arrived on the scene just in time to make airborne radar feasible for the British early in the war, giving Britain enough of an edge in antisubmarine and naval warfare to survive until the United States entered the war. Because of this new demand for polyethylene, ICI quickly built larger units for its production. In 1941, both information on the manufacture of polyethylene and its use in radar was transmitted to the United States, and DuPont built a plant to produce polyethylene under an ICI license [14].

Union Carbide independently developed a polyethylene process which was commercialized in 1943. The Union Carbide process used tubular reactors, while the early ICI design utilized stirred autoclave reactors. During the war, Germany developed polyethylene technology, based apparently on the ICI patents but using tubular reactors [14].

As late as 1943, the significance of polyethylene as a viable plastic was apparently not fully appreciated in technical circles. In the book Synthetic Resins and Rubber by P. O. Powers, published by Wiley in 1943, a table listed 42 of the significant synthetic polymer developments from 1831 through 1942. Polyethylene was not included, although a short paragraph in the book described the production and properties of high-pressure polyethylene. However, postwar developments quickly changed the stature of the first polyolefin plastic.

Following World War II, only DuPont and Union Carbide had polyethylene plants in the United States. That situation changed abruptly

when an antitrust suit resulted in a court decision in 1952 that ICI must license to all comers in the United States. Companies obtaining licenses within the next year were Dow Chemical, Eastman Kodak, and National Petrochemical. Spencer Chemical, Monsanto, and Koppers, with licenses from BASF in West Germany, also built high-pressure polyethylene plants which started up in 1954 and 1955. Meanwhile, Union Carbide and DuPont greatly expanded production facilities.

It was realized very early that the Union Carbide polyethylene differed in physical properties from the early ICI product, and Union Carbide polyethylene was preferred for certain critical applications during the war. It has since been learned that operating pressure and other conditions affect short-chain branching and density, and the type of reactor affects long-chain branching. Tubular reactors with plug flow apparently tend to produce less long-chain branching and so-called super molecules than autoclave reactors with back-mixing. Regardless of reactor type, operating pressure was generally 15,000-40,000 psig, and temperature was 150-250°C. A very small amount of oxygen or a peroxide was used as a free radical initiator to initiate and promote chain growth. Various chain transfer agents were used to modify molecular weight. Figure 1 depicts high-pressure polyethylene manufacture.

The density of early commercial polyethylenes was in the range of 0.910-0.925, and the crystalline melting point was about 115°C. The polymer was at first called polythene in England and simply polyethylene in the United States. However, the discovery and commercial development of low-pressure, catalytic processes in the

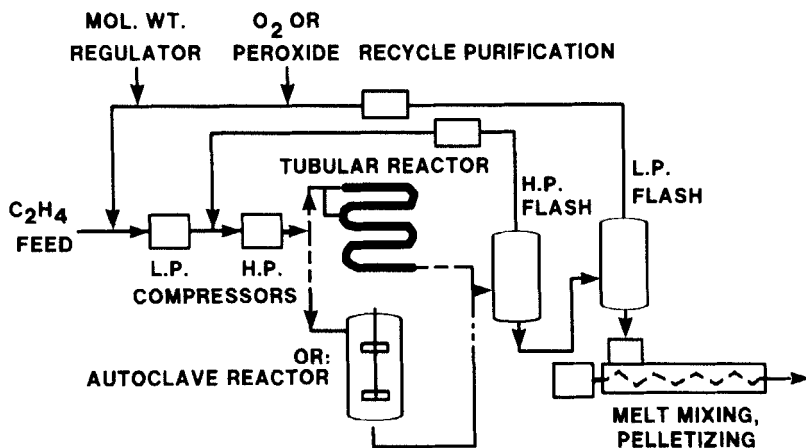


FIG. 1. High-pressure ethylene polymerization to LDPE.

1950s called for new nomenclature, since the new polyethylenes were quite different, having densities up to 0.97 and a crystalline melting point up to 135°C. Thus the "old" polyethylene began to be called high-pressure polyethylene (HPPE) or low-density polyethylene (LDPE), while the new type was called low-pressure polyethylene (LPPE) or high-density polyethylene (HDPE). Because of the essential absence of long-chain branching, it also began to be called linear polyethylene.

Polyethylene-Low Pressure Processes

Phillips Petroleum Company Process

Of the first low-pressure processes for polymerizing ethylene discovered in the early 1950s, the authors are, of course, able to give the most details on the Phillips commercial development. The Phillips polyethylene process, which in 1979 accounted for 1 billion pounds of polyethylene produced by Phillips Petroleum Co. alone at Pasadena, Texas, grew out of the discovery made in the Phillips laboratories in 1951 [23, 45]. By 1954, pilot plant studies had progressed far enough to permit commercial process design of a continuous process. By 1955, a 1000-lb per day semiworks plant was on stream. Being a scale-down of the commercial design, it was invaluable in the successful start-ups of the first commercial plants.

In April of 1955, Phillips management approved building a commercial complex, including an initial 75 million pounds per year HDPE plant and a 180 million pounds per year high-purity ethylene plant. However, it was concluded that no one manufacturer could develop the full market potential of the Phillips HDPE, and Phillips decided to license the process. In 1955 and 1956, nine companies in seven countries became licensees [46]. Each company was supplied with complete technical information and ground-up plant designs, and was furnished HDPE for evaluation and market development from the semiworks plant in Oklahoma.

Public disclosure (other than foreign patents) of details of the new Phillips process, information on structure of the polymer, and a survey of properties and expected applications came at the National ACS Meeting in April, 1956 [47-49].

The Phillips plant first produced polyethylene on December 31, 1956. Licensee plants were not far behind. The first commercial grades of HDPE produced by the Phillips process were homopolymers of less than 1 melt index. Ethylene-1-butene copolymers were introduced in 1958 [50], and soon other polymer parameters were utilized to extend the choice of polymer types. Production was entirely by the solution version of the process for the first 4 years [51]. The commercial plant process is depicted in Fig. 2. A liquid hydrocarbon stream containing cyclohexane is fed continuously with powdered catalyst, ethylene, and 1-butene comonomer as needed, to large

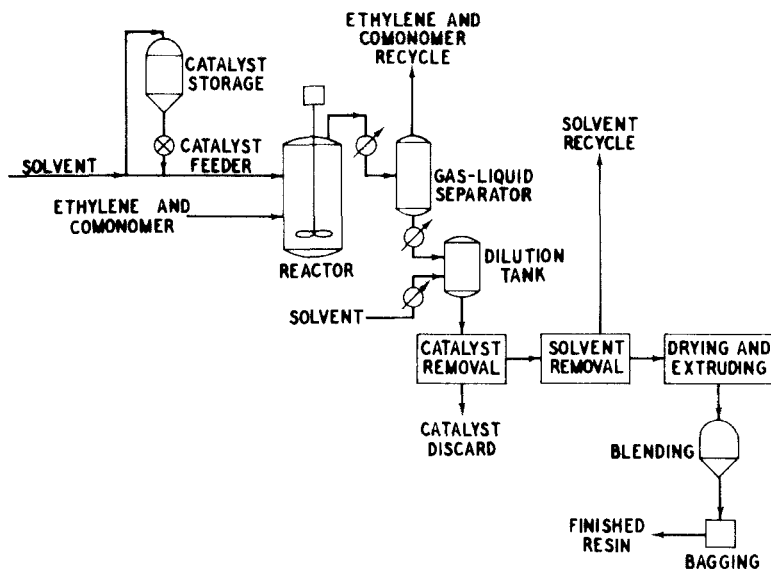


FIG. 2. Phillips original solution process (HDPE homopolymer and copolymer).

stirred reactors where polymerization takes place at temperatures of 125–175°C and pressures of 400–500 psig. Polymer solution is continuously withdrawn, flashed to remove ethylene, filtered or centrifuged to remove catalyst, steam stripped to remove solvent, dried, and pelletized. (A more recent system has no catalyst removal, and removes the solvent by flashing in devolatilizing extruders.)

Laboratory discoveries at Phillips in the early 1950s led to a slurry version of the process called the particle-form process [52, 53]. This system was commercialized in early 1961 and was quickly adopted also by licensees. It soon overtook the solution process in production capacity worldwide. The commercial particle-form process is depicted in Fig. 3. A low-boiling liquid isoparaffin is passed together with powdered catalyst, ethylene, and α -olefin comonomer to a loop reactor, which operates at an internal temperature of 70–100°C or higher and enough pressure to maintain liquid phase. A slurry of polymer and liquid hydrocarbon is discharged from a settling zone in the reactor to a flash tank, where hydrocarbon diluent and ethylene are recovered for recycle. The polymer crumb is freed of hydrocarbon and pelletized. Since catalyst yield is high, no catalyst removal step is used.

New copolymers containing 1-hexene comonomer and having new long-term properties were introduced in 1968. Although since 1958 we had been introducing short-chain branching with α -olefins and

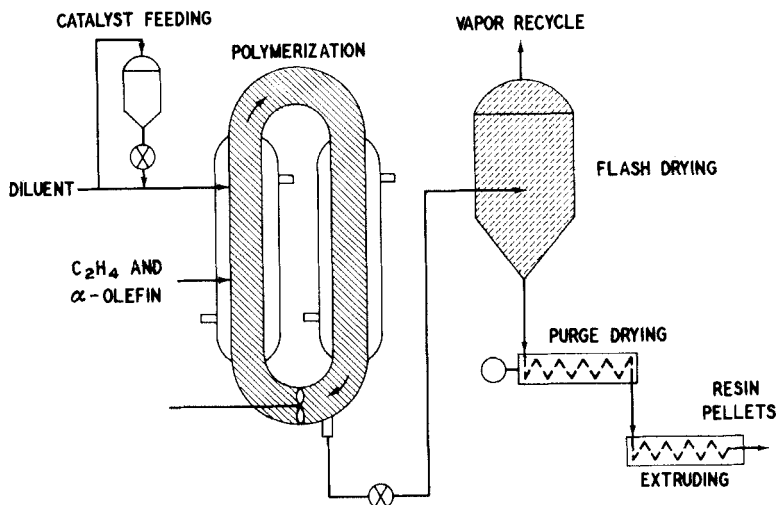


FIG. 3. Phillips particle-form process (HDPE and LDPE).

producing copolymers in the medium- and high-density ranges, we were not yet producing low-density polyethylene. But in 1969, Phillips announced to the press a new low-density process for producing polyethylene [54, 55]. Beginning in 1969, Phillips produced polymers with densities as low as 0.925 in a modified particle-form process.

Ziegler Process

Following discoveries by Karl Ziegler and co-workers in Germany in 1953 that polyethylene could be produced with titanium halides plus aluminum alkyls, Ziegler quickly began to license his patent. Starting in 1954, licenses were sold to Hoechst, Huels, and Ruhrchemie in Germany, Montecatini in Italy, Petrocarbon (later Shell) in Great Britain, Mitsui in Japan, and Dow, DuPont, Esso, Goodrich-Gulf, Hercules, Koppers, Monsanto, and Union Carbide in the United States. The license included use of Ziegler's patent and a 100-page manual describing a laboratory process. Each licensee had to develop a viable process from this meager information, which apparently did not include information on how to adequately control the molecular weight of the polyethylene.

The first commercial production of polyethylene in a Ziegler-type plant apparently occurred in the Hoechst plant in late 1956. A semi-works Koppers plant began polyethylene production for commercial use earlier in 1956. In the United States, Hercules went on stream first (1957), thus obtaining an early lead in Ziegler polyethylene, but later dropped out of polyethylene production in favor of polypropylene.

By 1960, production of polyethylene by Ziegler catalysts had reached about 70 million pounds in the United States. (Production of HDPE by Phillips and licensees in the United States in 1960 was nearly 200 million pounds.) Both slurry and solution processes, apparently involving both batch and continuous operation, were developed for the Ziegler catalysts. A problem with early continuous slurry processes was the build-up of "ivory" in the stirred autoclaves (slow polymer growth to large lumps in various poorly mixed zones in the reactors, requiring shut-down and cleaning). Polymerization is done at temperatures ranging from 50-120°C and pressures of 10-20 atm in the presence of paraffin diluents and hydrogen to control molecular weight [56, 57]. Catalyst deactivation in the reactor effluent, and catalyst decomposition and/or solution by methanol or various other polar compounds, is used to stop the reaction and purify the polyethylene product. Of particular concern is the removal of halides. Steam treatment of the polymer to remove catalyst components and solvents is sometimes practiced.

New supported Ziegler-type catalysts came into use in the early 1970s, increasing the catalyst efficiency and simplifying or eliminating the removal of catalyst. Several companies led by Solvay et cie [58], Montedison [59], and Mitsubishi [60], have announced the use of such catalysts. In general these catalysts involve a titanium compound supported on a magnesium salt or oxide and used with metal alkyl cocatalysts such as alkyl aluminum halides.

Standard Oil (Indiana) Process

Although the initial discovery of the synthesis of high polymers of ethylene over molybdena-promoted catalysts at the Standard Oil (Indiana) laboratories was a year earlier than the Phillips discovery, commercialization was much slower. A decision was made in 1958 to build polyethylene plants [61], and a plant built by Furukawa in Japan, of about 22,000,000 pounds annual capacity, went on stream in 1961 [62]. Later in the 1960s a plant utilizing the Standard process went on stream on the island of Sardinia.

These plants utilized a solution process at temperatures up to 300°C, requiring operating pressures up to 1000 psig. Molybdena-alumina catalysts were used [62, 63]. A plant built by Amoco in Texas went on stream in 1971, and probably used a chlorided molybdena-alumina catalyst [64]. However, because of economics, this plant was shut down in about 1973 and scrapped, apparently ending that Standard Oil (Indiana) process in the United States. (Amoco quickly built a new plant, having licensed Solvay- USI technology.)

Other, More Recent Low Pressure Processes

Modified Ziegler processes were announced in the 1960s and early 1970s that utilized modified Ziegler catalysts. Snam Progetti, Solvay,

Montedison, Mitsubishi, and Mitsui Petrochemicals announced slurry processes, and Stamicarbon announced a concentrated solution process.

Gas phase was studied at Phillips in the 1950s [65, 66], but the first gas-phase process was developed by Phillips licensee BASF in West Germany [67], where a small plant using Phillips catalysts was built in about 1964. Later in the 1960s Union Carbide, which had access to the BASF developments, developed a gas-phase process which was announced in the early 1970s. The Carbide gas-phase process using chromium-promoted catalysts was widely licensed in the 1970s, and a low-density gas-phase process was being licensed in the late 1970s [68].

Amoco recently started up a gas-phase process, based on Amoco technology, in Texas. Dow Chemical has recently announced commercialization of new low-density polyethylenes made in a low-pressure process which may be a solution process.

To sum up the status of LDPE and HDPE production in the United States up to 1980, Table 2 is presented. Shown are all current producers, with approximate production capacities and an indication of type of process being listed. Not shown are plants under construction. It is worth noting that polyethylene is by far the largest volume of all synthetic resins manufactured today. Polyethylene plants are now found in about 45 countries of the world.

Polypropylene

The first commercial production of polypropylene began in December 1957 by Hercules. Hoechst in West Germany and Montecatini (later Montedison) in Italy apparently started up polypropylene plants very soon thereafter [57, 69]. Thus polypropylene became a viable thermoplastic (and fiber) in 1958.

The earliest polypropylene plants used a slurry process in which a liquid diluent such as hexane or heptane was used, together with propylene, catalyst, and a small amount of hydrogen. The traditional catalyst has been a crystalline, violet colored form of $TiCl_3$ plus diethyl aluminum chloride as cocatalyst. The $TiCl_3$ has usually been made by the reduction of $TiCl_4$ with powdered aluminum, the final product being ball milled to generate the proper crystalline form to give high selectivity for the production of crystalline polypropylene. Another method of production is by the reduction of $TiCl_4$ with an aluminum alkyl [57].

The slurry processes involve polymerization in a stirred autoclave at temperatures below about $90^\circ C$ and at a pressure sufficient to maintain liquid phase with a 10-20% propylene concentration. The polymer forms as particles and is removed as a 20-40% solids slurry, which is flashed to remove propylene. The catalyst is deactivated and dissolved by means of an alcohol plus HCl or other polar organic compounds. Aqueous (or steam) extraction may also be used for

TABLE 2. United States Manufacturers of LDPE and HDPE, 1979

Manufacturer	Billions of lb, LDPE capacity	Process ^a	Billions of lb HDPE capacity	Process ^a
Allied Chemical	-	-	0.6	Phillips, Solvay
Amoco	-	-	0.35 ^b	Solvay-USI
Arco	0.4	ICI	0.35	Ziegler
Chemplex	0.3	USI, DuPont	0.3	Phillips
Cities Service	0.35	USI	0.2	Ziegler
Dart Industries	0.55	Own	-	-
Dow Chemical	1.0 ^c	Own	0.6	Own
DuPont	0.7	ICI, Own	0.45	Own
Eastman	0.25	ICI	-	-
Exxon	0.7	Dart	-	(To build Union Carbide Gas Phase)

POLYOLEFINS

Gulf Oil	0.85	Own (Spencer)	0.45	Phillips, Union Carbide
Hercules	-	-	0.02 ^d	Ziegler
Mobil	0.3	BASF	-	-
NPCC (USI)	0.7	Own	0.5	Phillips, Solvay-USI
Northern Petrochemical	0.65	BASF	-	-
Phillips Petroleum	(See HDPE)		1.0 ^e	Own
Soltex	-	-	0.6	Phillips, Solvay
Union Carbide	1.5	Own	0.45	Phillips, Own
Total	8.25		5.85	
Actual production, 1978	7.11		4.20	

^aProcess information based on early licensing arrangements plus later announcements.

^bIncludes gas-phase process plant developed by Amoco.

^cIncludes new low-pressure plant.

^dThe only ultrahigh molecular weight (UHMW) plant in the United States—now shut down.

^eIncludes capacity for up to 0.3 LDPE.

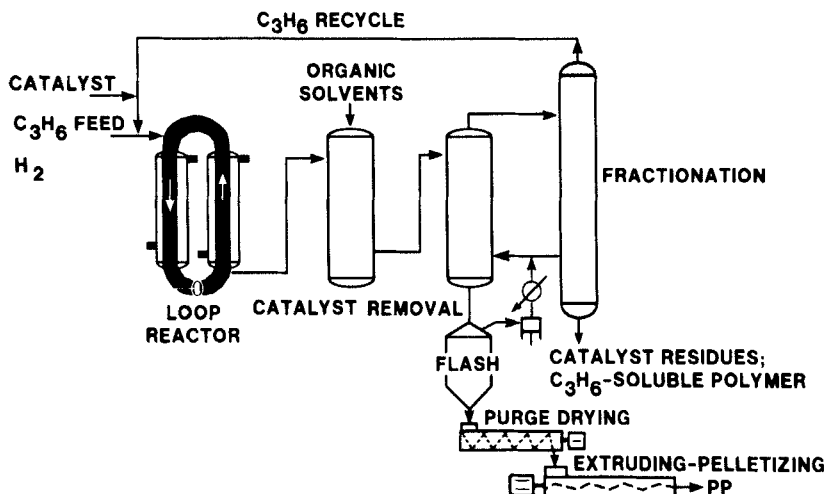


FIG. 4. Phillips bulk-slurry polypropylene process.

catalyst removal. Amorphous polypropylene, amounting to only a few percent, is removed as a solution in the liquid hydrocarbon which may be separated from the polymer by centrifuging or filtering [57].

Solution polymerization has been used commercially, including Texas-Eastman in the United States.

The first bulk polymerization system was commercialized by Phillips Petroleum Co. As shown in Fig. 4, a loop reactor is used in a slurry process in which liquid propylene is the only hydrocarbon diluent [70, 71]. In this process, catalyst is removed by solubilization with polar organic compounds which are washed from the granular polymer by a countercurrent stream of liquid propylene. The polymer is then separated from the propylene by flashing.

Dart Industries developed a bulk polymerization system in which liquid propylene is permitted to boil to remove the heat of reaction in a stirred vessel having vapor space in the top [57].

BASF put on stream a new gas-phase polypropylene plant in the mid-1960s in which mechanical stirring was relied on to prevent lumping in the reactor. High activity titanium catalysts reportedly avoided the need for catalyst removal, other than de-chloriding, but the products are higher than normal in amorphous content [57]. Northern Petrochemical licensed this process and began operations in the United States in the mid-1970s. Very recently, Amoco has apparently put on stream a large new gas-phase plant in Texas, based on technology developed by Amoco.

Before the 1970s, catalyst activity in commercial processes was fairly low. Solvay developed a higher activity $TiCl_3$ catalyst in which $TiCl_4$ is converted to a highly specific $TiCl_3$ through a four-step

TABLE 3. United States Manufacturers of Polypropylene, 1979

Manufacturer	Plant capacities (millions of lb/yr)	Process, catalyst information
Amoco	830	Slurry and Amoco gas-phase processes
Arco Polymers	400	Bulk (Phillips) process (Mitsui P.-Montedison catalyst license)
Dart Industries	300	Bulk-boiling process
Exxon	550	Slurry
Gulf Oil	400	Slurry
Hercules	1,150	Slurry (Solvay catalyst license)
Northern Petrochemical	200	Gas-phase process (BASF)
Novamont	430	Slurry process (Mitsui-Montedison)
Phillips	200	Bulk slurry (Phillips)
Shell Chemical	600	Slurry
Soltex	200	Slurry (Solvay process)
Texas Eastman	140	Solution process
Total	3,700	
Production in U.S. in 1978	3,074	

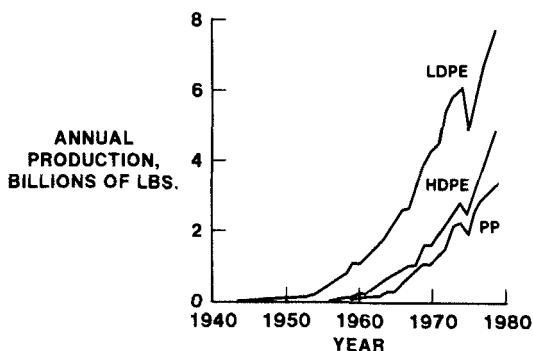


FIG. 5. United States production of low- and high-density polyethylene and polypropylene (U.S. Trade Commission).

process [72]. This catalyst decreases the amount of catalyst residues to be removed but does not eliminate the need for catalyst removal entirely. More recently, Montedison [73] and perhaps others have developed supported titanium catalysts which decrease and may soon eliminate the need for catalyst removal. These catalysts generally have some form of magnesium halide as an ingredient.

The brittleness temperature of crystalline polypropylene is about 15°C , with the result that the low-temperature impact resistance of the thermoplastic is poor. Impact resistance grades of polypropylene were developed in the 1950s at Phillips [74] through the introduction of ethylene polymer blocks. The addition of elastomers and polyethylene by melt blending also improves the low-temperature properties. Random copolymers containing 2-3% ethylene are also made to lower the modulus.

Table 3 summarizes the status up to 1980 of production of polypropylene in the United States, showing manufacturers, an estimate of capacity, and information on the process.

Figure 5 shows the growth of the major polyolefins, LDPE, HDPE, and polypropylene (PP) in the United States since start-up of the first plants. What the 1980s will bring is anybody's guess, but predictions of about 8% annual growth in the near future are common.

OTHER POLYOLEFIN PLASTICS

Poly-1-butene

The commercialization of poly-1-butene plastic has been fraught with uncertainty, to say the least. Petrotex Corp. began commercial development of poly-1-butene in about 1963 with a 2000 lb/day semi-works plant, which was operated until about 1966 before it was

abandoned as unpromising [75]. Mobil Chemical Co. started up a 4 million pound per year poly-1-butene plant in Texas in 1967. However, Mobil later decided not to proceed and licensed the Mobil technology to Witco Chemical Corp. in 1972 [75, 76]. Witco built a 50-million lb/yr plant in Louisiana, which began start-up operations in 1975, with difficulties. The plant was sold to Shell in late 1977 [77], and Shell has been working to bring the plant toward rated capacity. Apparently, about 25 million pounds were produced in 1978.

The Shell plant uses a bulk polymerization process and a "Ziegler-Natta" catalyst at 40-90°C and enough pressure to maintain liquid phase. Hydrogen is added to the stirred reactor to control molecular weight. Catalyst removal is required, but there is no removal of amorphous polymer.

Huels AG, West Germany, began operation of a poly-1-butene plant in 1971. This plant had a rated capacity of 26 million lb/yr by 1973. The Huels process uses a hydrocarbon solvent, and some amorphous polymer is separated from the product [78].

Poly-1-butene is a unique polyolefin because of its slow (4-8 day) transition from one crystalline form to another harder one. It is of particular interest in pipe applications and in heat-resistant film. Both the polymerization problems (it forms neither a true slurry nor a trouble-free solution) and the slow crystalline change problem has slowed its commercial growth up to 1980.

Poly(4-methyl-1-pentene)

The high melting point and extreme clarity of crystalline poly(4-methyl-1-pentene) made it of interest for commercial development. ICI started commercial development in 1965 and began production of polymethyl pentene (PMP) in a 4.5 million lb/yr plant in England in 1968 [79]. The ICI version of PMP is principally made of 4-methyl-1-pentene but contains minor amounts of α -olefin. The comonomer enhances clarity and other physical properties. Ziegler-type catalysts similar to those used for propylene polymerization are used. Polymerization is at temperatures and pressure near ambient and can be done in the bulk or with added inert hydrocarbons.

Since 1975, PMP has been manufactured (on a fairly small scale) solely by Mitsui Petrochemical Industries, Japan, by license from ICI [80]. Some of the applications are laboratory and medical ware such as throw-away syringes and cook-in-bag food packaging.

Though compounds of the nature of polyolefins can be said to have been known for more than 80 years and the subject of quite intensive work for nearly 50 years, more information on products, processes, and catalyst continues to be developed. Nimble minds will no doubt continue to produce new and useful information on this broad subject for many years to come.

REFERENCES

- [1] R. A. V. Raff, in Encyclopedia of Polymer Science and Technology, Vol. 6 (N. M. Bikales, ed.), Wiley-Interscience, New York, 1967, p. 276.
- [2] C. E. H. Bawn and A. Ledwith, in Encyclopedia of Polymer Science and Technology, Vol. 10 (N. M. Bikales, ed.), Wiley-Interscience, New York, 1969, p. 344.
- [3] E. Hinderman, Dissertation, Zurich, 1897.
- [4] H. von Pechman, Ber., **31**, 2643 (1898).
- [5] E. Bamberger and F. Tschirner, Ibid., **33**, 955 (1900).
- [6] J. Hertzog and R. Schonbach, Monatsh., **33**, 677 (1912).
- [7] H. Meerwein and W. Burneleit, Ber., **618**, 1840 (1928).
- [8] W. Werle, Dissertation, Marburg, 1938.
- [9] Phillips Petroleum Company, previously unpublished data.
- [10] H. Hoberg and K. Ziegler, Brennst.-Chem., **39**, 302 (1958).
- [11] H. Pichler, Ibid., **19**, 226 (1938).
- [12] H. Pichler and H. Buffleb, Ibid., **21**(24), 285 (1940).
- [13] R. A. V. Raff and E. Lyle, in High Polymers, Vol. 20, Part 1 (R. A. V. Raff and K. W. Doak, eds.), Wiley-Interscience, New York, 1965, p. 8.
- [14] J. C. Swallow, in Polythene, 2nd ed. (A. Renfrew and P. Morgan, eds.), Interscience, New York, 1960, pp. 1-10.
- [15] C. W. Bunn, Trans. Faraday Soc., **35**, 482 (1939).
- [16] E. W. Fawcett, R. O. Gibson, M. W. Perrin, J. G. Patton, and E. G. Williams (to ICI), British Patent 471,590 (Accepted September 6, 1937).
- [17] J. J. Fox and A. E. Martin, Trans. Faraday Soc., **36**, 897 (1940).
- [18] G. D. Buckley, L. H. Cross and N. H. Ray, J. Chem. Soc., p. 2714 (1950).
- [19] G. D. Buckley and N. H. Ray, Ibid., p. 3701 (1952).
- [20] N. W. Krase (to DuPont), U.S. Patent 2,396,791 (Issued 1946; Filed 1942).
- [21] A. W. Larcher and D. C. Pease (to DuPont), U.S. Patent 2,816,883 (Issued 1957; Filed 1951).
- [22] A. Zletz [to Standard Oil Co. (Indiana)], U.S. Patent 2,692,257 (Issued 1954; Filed April 28, 1951).
- [23] J. P. Hogan and R. L. Banks (to Phillips Petroleum Co.), Belgian Patent 530,617 [Filed January 24, 1955 (Filed in United States January 27, 1953, Serial Number 333,576)]; Australian Patent Application 864/54 (Filed August 6, 1954).
- [24] K. Ziegler, H. Breil, H. Martin, and E. Holzkamp (to K. Ziegler), German Patent 973,626 (Issued April 14, 1960; Filed November 17, 1953); see also U.S. Patent 3,257,332 (Issued June 21, 1966; Filed November 15, 1954).
- [25] K. W. Doak and A. Schrage, in High Polymers, Vol. 20, Part 1 (R. A. V. Raff and K. W. Doak, eds.), Wiley-Interscience, New York, 1965, p. 351.

- [26] Consolidated Civil Action No. 4319, Federal District Court (Delaware) (consolidation of civil actions filed in 1972).
- [27] Karl Ziegler testimony, Civil Action 3-2225, Federal District Court (Northern District of Texas, Dallas), May 10, 1971.
- [28] C. W. Bunn, in Polythene, 2nd ed. (A. Renfrew and P. Morgan, eds.), Interscience, New York, 1960, p. 98.
- [29] Interference No. 89,634, initiated by the U.S. Patent and Trademark Office, September 9, 1958.
- [30] G. Natta, J. Polym. Sci., 16, 143 (1955).
- [31] G. Natta (to Montecatini), Italian Patent Application 24,227 (Filed June 8, 1954); G. Natta, P. Pino and G. Mazzanti, Italian Patent Application 25,109 (Filed July 27, 1954).
- [32] W. N. Baxter, N. G. Merckling, I. M. Robinson, and G. S. Stammstoff (to DuPont), U.S. Patent Application S.N. 451,064 (Filed August 19, 1954).
- [33] A. Zletz [to Standard Oil (Indiana)], U.S. Patent Application S.N. 462,480 (Filed October 15, 1954).
- [34] C. A. 4319, Federal District Court (Delaware), (a) Exhibit P-56; (b) Exhibit P-40.
- [35] G. Natta, P. Pino, and G. Mazzanti (to Montecatini), U.S. Patent Application S.N. 514,099 (Filed June 8, 1955).
- [36] G. Natta, P. Pino, G. Mazzanti, P. Corradini, and U. Gianini, Rend. Accad. Naz. Lincei, 19, 397 (1955).
- [37] G. Natta, P. Corradini, and I. W. Bassi, Ibid., 19, 404 (1955).
- [38] G. Natta, Angew. Chem., 68, 393 (1956).
- [39] A. C. Haven, Jr. (to DuPont), U.S. Patent 3,257,367 (Issued June 21, 1966; Filed June 23, 1955).
- [40] T. Alfrey, A. Bartovics, and H. Mark, J. Am. Chem. Soc., 65, 2319 (1943).
- [41] M. L. Huggins, Ibid., 66, 1991 (1944).
- [42] C. E. Schildknecht, S. T. Gross, H. R. Davidson, J. M. Lambert, and A. O. Zoss, Ind. Eng. Chem., 40, 2104 (1949).
- [43] G. Natta, I. W. Bassi, and P. Corradini, Makromol. Chem., 18-19, 455 (1955).
- [44] G. Natta and F. Danusso (ed.), Stereoregular Polymers and Stereospecific Polymerizations, Pergamon, New York, 1967, two volumes.
- [45] J. P. Hogan, Chemist, 50(2), 46 (1973).
- [46] J. P. Hogan, in High Polymers, Vol. 18 (G. Ham, ed.), Wiley-Interscience, New York, 1964, p. 111.
- [47] A. Clark, J. P. Hogan, R. L. Banks, and W. C. Lanning, Ind. Eng. Chem., 48, 1152 (1956).
- [48] R. V. Jones and P. J. Boeke, Ibid., 48, 1155 (1956).
- [49] D. C. Smith, Ibid., 48, 1161 (1956).
- [50] J. E. Pritchard, R. M. McGlamery, and P. J. Boeke, Mod. Plast., 37, 132 (1959).
- [51] A. Clark and J. P. Hogan, in Polythene, 2nd ed. (A. Renfrew and P. Morgan, eds.), Interscience, New York, 1960, p. 29.
- [52] R. G. Rohlfing (to Phillips Petroleum Co.), U.S. Patent 3,226,205 (1965).

- [53] D. D. Norwood (to Phillips Petroleum Co.), U.S. Patents 3,248,179 and 3,257,362 (1966).
- [54] Chemical and Engineering News, 47(17), 15 (1969).
- [55] J. P. Hogan (to Phillips Petroleum Co.), U.S. Patent 3,666,736 (1972).
- [56] E. J. Vandenberg (to Hercules), U.S. Patent 3,051,690 (1962).
- [57] E. J. Vandenberg and B. C. Repka, in High Polymers, Vol. 29 (C. E. Schildknecht and I. Skeist, eds.), Wiley-Interscience, New York, 1977, p. 337.
- [58] J. Stevens, Hydrocarbon Processing, 49(11), 179 (1970).
- [59] Hydrocarbon Processing, 50(11), 195 (1971).
- [60] A. Kageyama and A. Hirtani, Hydrocarbon Process., 51(11), 97 (1972).
- [61] Chemistry in the Economy, American Chemical Society, Washington, D.C., 1973, p. 71.
- [62] E. L. D'Ouville, in Polythene, 2nd ed. (A. Renfrew and P. Morgan, eds.), Interscience, New York, 1960, p. 35.
- [63] Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., Vol. 14, Wiley, New York, 1976, p. 255.
- [64] O. O. Juveland, E. F. Peters, and J. W. Shepard, Polym. Prepr., 10(1), 263 (April 1969).
- [65] W. C. Lanning, J. P. Hogan, R. L. Banks, and C. V. Detter (to Phillips Petroleum Co.), U.S. Patent 2,970,135 (1961).
- [66] R. F. Dye (to Phillips Petroleum Co.), U.S. Patent 3,023,203 (1962).
- [67] K. Wisseroth, Angew. Makromol. Chem., 8(88), 41 (1969).
- [68] Hydrocarbon Processing, 59(11), 227 (1979).
- [69] Hercules Mixer, 41, 1-10 (January 1958).
- [70] A. A. Harban, J. A. Delap, and C. W. Moberly (to Phillips Petroleum Co.), British Patent 940,178 (1963).
- [71] C. G. Houser, J. Mitacek, R. G. Rohlring, and W. E. Payne (to Phillips Petroleum Co.), U.S. Patent 3,203,943 (1965).
- [72] J. P. Hermans and P. Henriquille (to Solvay), German Patent Application 2,213,086 (1972).
- [73] U. Giannini, A. Casata, P. Lorgi, and R. Mazzocchi (to Montedison), German Patent Application 2,346,577 (1974).
- [74] J. T. Edmonds (to Phillips Petroleum Co.), U.S. Patents 3,970,719 (1976) and 4,039,632 (1977).
- [75] J. C. Davis, Chem. Eng., 80(3), 32 (1973).
- [76] Chemical Engineering, 81(3), 23 (1974).
- [77] Plastics Engineering, 34(10), 43 (1978).
- [78] M. D. Rozenzewig, Chem. Eng., 80(3), 56 (1973).
- [79] M. R. Day, Mod. Plast. Encycl., 45(14A), 220 (1968).
- [80] Y. Tanabarashi, Ibid., 54(10A), 76 (1977).