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Polyolefins

Processing, Structure Development, and Properties

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The Authors:
Professor Dr. James L. White and Dr. David D. Choi, Department of Polymer Engineering,
The University of Akron, 250 South Forge Street, Akron, OH, 44325-0301, USA
(Dr. David D. Choi is currently with Asahi Thermofil, inc.; One Thermofil Way, Fowlerville, MI 48836, USA)

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Preface

Polyolefins, i.e., the polymers synthesized from olefinic monomers, are the major commercial thermoplastics. They are also important components of major thermoplastic elastomers. Polyethylene and polypropylene are the two largest thermoplastics in volume and are fabricated into filaments, films, and molded parts.

The book treats the history, commercialization, characterization, and crystallography of various commercial polyolefins and polystyrenes and describes development of structure during fabrication of these polymers into various shapes. It is in this latter area that this book is unique. No other volume describes the structuring of molten polyolefins in fiber, film, and molding processes with correlations between structural order such as crystalline unit cell, polymorphic effects and orientation with processing parameters.

We have incorporated polystyrene into this book although it is not classified as a polyolefin, but rather as an aromatic vinyl polymer. The structure and behavior of its isotactic and syndiotactic forms are similar to those of the corresponding polyolefins and help the drawing of conclusions. Atactic polystyrene vitrifies into a glass (solidified melt) and lets us know the fundamentals of structuring in polymers prior to crystallization in polymer processing operations.

Throughout the book we made direct comparisons of the structure and behavior of polyethylene, isotactic and syndiotactic polypropylenes, isotactic polybutene-1, isotactic poly(4-methyl pentene-1), and the different polystyrenes. This book should be of interest to engineers, chemists, and technologists working with polyolefins.

The book was written while both authors were affiliated with the Department and Institute of Polymer Engineering at the University of Akron.

James L. White
David Dongman Choi

We dedicate this book
to our wives
Alganesh Tereste White
and
Hyeon Park Choi

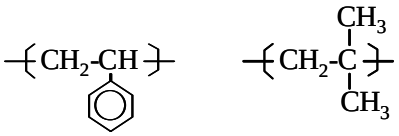
Contents

1 Origins of Polyolefins

1.1 Introduction and Prehistory

In this chapter, the invention and commercial development of several important polyolefins, especially crystalline polyolefin thermoplastics will be described. We will consider the development of low density polyethylene (LDPE) in the 1930s and continue with high density polyethylene (HDPE) and the isotactic polyolefins of the 1950s and later, and will also briefly discuss ethylene-propylene rubber. We will also describe the newer metallocene syndiotactic polyolefins and cyclopolyolefins of the 1980s and 1990s. It is presumed that the reader is aware of various features of polyolefin structure including tacticity and branching. Details on these structural features are given in Chapter 2.

It is useful to begin with some perspective. It was only in the 1920s with the efforts of H. Staudinger [1, 2] that the structure of polymers as long chain molecules was elucidated. The importance of the ability to synthesize these materials and their commercial possibilities were realized by industrial firms around the world. The leading company in this regard, which was cited by Staudinger in his book [2], was the German I. G. Farbenindustrie (a combine of Farbenfabriken Bayer, BASF and Farbwerke Hoechst created in 1925). It developed atactic polystyrene, polyvinyl chloride, butadiene-acrylonitrile rubber, and butadiene-styrene rubber in subsequent years. Also commercialized was the relatively small volume polyolefin elastomer, polyisobutylene. The two early I. G. Farbenindustrie hydrocarbon polymers were:



(1-I)

Both of these were primarily manufactured in the old BASF facility in Ludwigshafen. The I. G. Farbenindustrie activities and those of the American E. I. du Pont de Nemours were also much more aggressive than initially those for polyethylene, which we will presently discuss. The 1950s were to be the major period of polyolefin development.

1.2 Polyethylene

1.2.1 Low Density Polyethylene

The development of a commercial polyethylene was due to the efforts of the large English chemical company, Imperial Chemical Industries [3, 4], in the 1920s and 30s to make use of the high pressure chemistry based on the activities of Prof. A. Michels in Amsterdam. Based on his activities, research was established at the ICI Dyestuff Division in the early 1930s in Winnington, England. The high pressure apparatus was delivered, and work began in 1931. The principal researchers were E. W. Fawcett and R. O. Gibson. A 1934 paper by Fawcett and Gibson [5] describes their research perspectives.

In some of their experiments, ethylene was heated under pressure in the range of 1000 to 2000 atmospheres. Although traces of white powder were found, they were not recognized as polyethylene. Subsequently, Fawcett and Gibson sought to react ethylene and benzaldehyde at 1960 atmospheres and 170 °C. A waxy solid substance was produced and its analysis was found to have the empirical formula CH_2, that is

$$-\left(CH_2\right)_n- \quad \text{or} \quad -\left(CH_2\text{-}CH_2\right)_n- \tag{1-II}$$

The experiment was difficult to reproduce, and their efforts were discontinued in March 1933.

Later, work began using a new apparatus, which possessed greater safety characteristics. The new generation of experiments involved M. W. Perrin and J. G. Paton. Perrin, like Gibson, had worked with Michels in Amsterdam. Perrin and Paton began their experiments in December 1935 and soon, by using conditions similar to Fawcett and Gibson, produced high-molecular weight polyethylene. At higher pressures (3000 atmospheres), they obtained higher conversions. It came to be realized that some oxygen was needed as a polymerization initiator. ICI filed a provisional patent specification in February 1936 in the names of Fawcett, Gibson, Perrin, Paton and Williams [6]. The density of this polyethylene was 0.91 g/cm^3.

ICI soon decided to scale up and commercially produce polyethylene. Compressors to continuously deliver ethylene at pressures up to 3000 atmospheres were ordered. These were to be designed by Michels, and a pilot plant was built in Winnington. The pilot plant ran intermittently until March 1938. Commercial production began at the Wallersford Works in May 1938. One ton of polyethylene was produced in 1938, 10.5 tons in 1939, 106 tons in 1940 and 576 tons by 1942.

In a 1940 paper, Fox and Martin [7] showed by infrared spectroscopy that there were more methyl groups in the ICI high pressure polyethylenes than could be accounted for by chain ends. This led to the realization that these polyethylenes had significant amounts of branching.

Dupont obtained a license from ICI to produce polyethylene. During World War II alternate processes for producing free radical polyethylene were developed by the I. G. Farbenindustrie in Germany (Ludwigshafen) and by Union Carbide in the United States.

At this time, low density polyethylene was primarily used for film packaging.

1.2.2 Karl Ziegler and High Density Polyethylene

Karl Ziegler was a pioneer of organometallic polymerization. He had been a doctorate student of Karl von Auwers at the University of Marburg. It was known that metals, such as sodium, could polymerize butadiene and similar monomers. BASF in Ludwigshafen had practiced such polymerization during World War I. Ziegler's efforts to synthesize organometallic compounds and polymerize new polymers with them date to the early 1920s. He became interested in the alkyl compounds of potassium and sodium [8]. Ziegler obtained a position at the University of Heidelberg in 1927. Shortly thereafter, Ziegler and Bahr [9] published a study, which showed that oligomers and polymers of butadiene and styrene can be produced using alkali alkyls.

In 1930, Ziegler and Colonius [10] synthesized alkyl lithium compounds including butyl lithium. In subsequent years, Ziegler and his coworkers [11–13] polymerized various hydrocarbons with organo lithium, sodium, and potassium initiators. Special emphasis was given to polymerization of butadiene. During this period, Ziegler et al. [13] discovered the phenomenon of 'living polymerization' with alkyl lithium initiators. It is possible that Ziegler in this period was influenced by synthetic rubber activities at the I. G. Farbenindustrie (BASF) in nearby Ludwigshafen. In the 1950s, Ziegler's alkyl lithium initiator became widely used in the synthetic rubber industry in the manufacture of polybutadienes, polyisoprenes, and butadiene-styrene copolymers of controlled micro-structure. The living polymerization technique was subsequently used to make block copolymers.

In 1937 Ziegler moved from the University of Heidelberg to the University of Halle/Saal [14]. In 1943, he became the director of the Institut für Kohleforschung in Mülheim near Essen and Cologne (Köln). Here he was asked to transfer his polymerization efforts from butadiene to ethylene. Not surprisingly, he began his research using ethyl lithium. With ethyl lithium, he was able to polymerize higher linear chain alkyls and the

corresponding alcohols and acids [8, 15]. There were, however, unlike in the polymerization of butadiene, limitations to the molecular weight that could be achieved before degradation of the active site. Ziegler and Gellert [8, 15] then used the newly introduced $LiAlH_4$ as an initiator and found that they could achieve higher molecular weights.

From the late 1940s, Ziegler and his coworkers turned their attention to synthesizing aluminum alkyls [8, 16] and using them as initiators for polyethylene. Ziegler was encouraged enough to file patent applications with Gellert [17] as early as 1950 (in Germany) on polymerization of ethylene with aluminum trialkyls as well as alkyls of beryllium, gallium and indium.

These 'Aufbau' reactions of Ziegler attracted the attention of the Italian firm Montecatini and Giulio Natta of Milan Politechnico. Montecatini took out a license on Ziegler and Gellert's patent as did Farbwerke Hoechst in Frankfurt-am-Main and the American Hercules Powder Company [18]. As a part of the Montecatini agreement, Natta was able to place research assistants in Ziegler's Mülheim laboratory at this time.

However, inconsistent results were obtained in the Ziegler-Gellert system. The cause was traced to impurities in the reaction system such as nickel. Ziegler and his colleagues then looked for co-catalysts to use with the aluminum alkyls. Titanium containing co-catalysts were found to be most effective. Ziegler and his colleagues [19, 20] reported the development of the Ziegler-Mülheim process in papers published in 1954 and 1955.

Ziegler's polyethylene differed from ICI's material in having a higher density and a higher crystalline melting temperature. Its tensile modulus and tensile strength were also much higher. Ziegler and his coworkers concluded that they had made a linear polyethylene. Ziegler, H. Breil, E. Holzkamp, and H. Martin began filing patents around the world in November 1953. The patents were assigned to Ziegler. The first patent was filed in Germany, then elsewhere and about a year later in the USA [21]. Ziegler et al.'s patent claims a catalyst of aluminum trialkyl with salts, oxides, or hydroxides of metals of the Periodic Table groups IV-B, V-B and III-B. Ziegler et al.'s US patent included the initiators

- aluminum trialkyl-titanium tetrachloride,
- aluminum trialkyl-zirconium acetylacetonate,
- aluminum trialkyl-thorium acetylacetonate,
- aluminum trialkyl-uranium tetrachloride,
- aluminum trialkyl-vanadium acetylacetonate,
- aluminum trialkyl-chromium acetylacetonate,

- aluminum trialkyl-tungsten hexachloride,
- aluminum trialkyl-molybdenum acetylacetonate,
- aluminum trialkyl-zirconium tetrabromide,
- aluminum trialkyl K_2TiF_6, and
- aluminum trialkyl-zirconium tetrabutylate.

Farbwerke Hoechst (later Hoechst A. G. and more recently Celanese A. G./Ticona), BASF A. G., Farbenfabriken Bayer A. G., and Chemische Werke Hüls were the successors of the I. G. Farbenindustrie. Farbwerke Hoechst was already in contact with Karl Ziegler as described earlier. They obtained a license from him in August 1954 and became the first manufacturer of the Ziegler high density linear polyethylene. A large manufacturing plant producing 250 tons (500,000 lbs) per month was in operation at the end of 1955 [22].

Other licenses went to Chemische Werke Hüls (later part of Degussa) and Ruhrchemie in Germany, Montecatini in Italy, and Dow Chemical, Du Pont, Esso (later Exxon and more recently Exxon Mobil), Hercules, Koppers, and others in the United States. Koppers began a semi-works plant in the United States in 1956, and Hercules a full scale plant in 1957.

1.2.3 Standard Oil of Indiana

At this time, various industrial companies were involved in trying to polymerize ethylene. Zletz [23] of Standard Oil of Indiana (later Amoco and subsequently BP Amoco) described in an April 1951 patent application of the polymerization of ethylene with molybdenum oxide-aluminum oxide initiators. Compounds such as cobalt-molybdate were probably involved. Products from greases to tough resins were produced, but little information, if any, was given in the patent about the structure of the resin. It appears to have been a linear polyethylene. These activities were only slowly followed up.

1.2.4 Phillips Petroleum and High Density Polyethylene

In the 1940s, Bailey and Reid [24] of Phillips Petroleum (later Conoco Phillips) in Bartlesville, Oklahoma, USA found that ethylene could be polymerized to liquid polymers over certain nickel oxide-silica-alumina catalysts. Subsequently, Hogan and Banks [25]

building on this work polymerized ethylene to solid polymers using chromium oxide-silica-alumina catalysts. Chromium oxide with zirconium oxide and thorium oxide were also discussed. The polymerization product was proved to be a linear high density polyethylene [25, 26]. Phillips filed a patent application on January 24, 1953 [25]. Later patents by Hogan and Banks [27, 28] describe initiators based on chromium oxide and strontium oxide [27] and chromium oxide with various additives [28].

Applications research and market development began in 1955. A 1000 lbs (0.5 ton) per day semiworks plant was put into operation in Bartlesville [29]. In April 1955, Phillips Petroleum approved the building of a polyethylene plant in Pasadena, Texas with a production capacity of 6.5 million lbs per month [29]. Phillips Petroleum moved into commercial production of high density polyethylene in 1956 [29].

Licenses were given in 1955–1956 to nine different companies in seven countries to produce high density polyethylene according to the Phillips process.

A 1956 paper by Jones and Boeke [30] describes the new Phillips Marlex® 50 polyethylene with a density of 0.96 g/cm^3 as opposed to 0.92 g/cm^3 for conventional high pressure branched polyethylene and a melting point of 135 °C as opposed to 110 °C.

By this time, the older ICI type polyethylene was becoming called low density polyethylene (LDPE), and the newer materials made by Ziegler and Phillips catalysts were called high density polyethylene (HDPE).

1.2.5 Linear Low Density Polyethylene

Phillips Petroleum seems to have begun research on ethylene copolymers quite early, and they are cited in the original Hogan and Banks patent [25]. By 1958, Phillips was commercially manufacturing high to moderate density ethylene-butene copolymers.

As early as 1957, DuPont researchers filed patents [31, 32] on copolymers of ethylene with varying amounts of 1-butene, 1-pentene, 1-hexene, 1-octene, and higher α-polyolefins such as 1-decene and 1-octadecene with a Ziegler type catalyst. These new copolymers had densities similar to the ICI LDPE (~0.92 g/cm^3). The best mechanical and optical performance in the copolymers was found for the higher olefin comonomers including 1-octene, 1-decene, and higher α-olefins. DuPont researchers considered also a terpolymer with ethylene and two minor monomers, one a higher olefin such as octene and the other a lower olefin such as propylene.

These new polymers were called linear low density polyethylene (LLDPE) to distinguish them from LDPE. Crystallinity reduction came from the comonomers.

Phillips Petroleum began to manufacture ethylene-hexene copolymers with densities of 0.92 g/cm^3 in 1968. Linear low density polyethylene was developed widely commercially in the 1970s, notably by a process technology developed by Union Carbide.

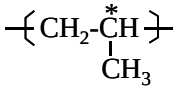
LLDPE has come to increasingly supplant the ICI type LDPE.

1.3 Isotactic Polypropylene

1.3.1 Giulio Natta, Milan Politechnico and Montecatini

Natta had research assistants in Ziegler's Mülheim laboratory from 1950 and became very familiar with his polymerization systems [18]. He was aware that Ziegler had tried to polymerize polypropylene but had not considered it successful. In 1953–1954, Ziegler sold pails of his catalysts to various industrial firms. Among those obtaining catalysts was the Montecatini company based in Milan, Italy. Montecatini made arrangements with Prof. Giulio Natta and his coworkers to apply these catalysts to a range of monomers. Natta, on receiving the catalysts, immediately turned his attention to polypropylene.

Natta et al. made rapid progress with polypropylene.



(1-III)

Polypropylene with its asymmetric carbon atoms (C*) was known at the time as a rubbery waxy non-crystalline material. The new discoveries were quite striking. Staudinger [2] in his 1932 monograph had noted the occurrence of the large number of stereoisomeric groups in polymers due to asymmetric carbon atoms in polystyrene and other vinyl polymers. In 1942, Bunn [33] with ICI had imagined stereoregular vinyl chains and sought to predict their structures in crystals. The early Natta polypropylenes prepared were rubbery and waxy but contained hard white materials [18], which were found to be crystalline. The first crystalline polypropylenes were synthesized by Natta et al. in March 1954. Further X-ray diffraction investigations and model built by Natta and Corradini showed that all of the asymmetric carbon atoms had the same symmetry. The new polypropylene was called 'isotactic' (roughly same placement) following the suggestion of Natta's wife (see Section 2.2.2). The isotactic polypropylene chain structure was the same as the one proposed by Bunn [33].

Natta together with P. Pino and G. Mazzanti began filing patents [34] in June 1954. They claimed a stereoregular crystalline polypropylene polymerized by Ziegler type catalysts. The examples include initiator systems

- aluminum triakyl-titanium tetrachloride,
- aluminum trialkyl-titanium tetrabromide,
- aluminum trialkyl-vanadium tetrachloride,
- aluminum trialkyl-zirconium tetrachloride, and
- aluminum trialkyl-chromium acetylacetonate.

The US patent, which did not issue until 1973 was assigned to Montecatini Edison, the successor company of Montecatini.

Ironically, Ziegler soon synthesized a crystalline polypropylene with his catalyst. However, when he discovered the Natta-Pino-Mazzanti patent application, he withdrew his claim and supported Natta.

In 1954–1955, Natta and his coworkers [35–37] submitted a series of papers in which they announced the synthesis of the new crystalline polypropylene. It had a density of 0.91 g/cm^3 and a crystalline melting temperature of about 165 °C.

Production of isotactic polypropylene was initiated by Montecatini in Brindisi, Italy in 1957. Farbwerke Hoechst and Hercules began production of isotactic polypropylene with Montecatini licenses in 1957 and 1958. It has since become the world's major thermoplastic second only to polyethylene. Hercules and Montecatini later merged their operations to form Himont. This company in turn joined with Shell to form Montell. BASF later joined this combine to form Basell.

There was a long period of catalyst development and improvement to make isotactic polypropylene. The problem was to achieve both high yield and high tacticity [38, 39]. This has involved various generations of what may be called Ziegler-Natta catalysts.

1.3.2 Standard Oil of Indiana and Phillips Petroleum

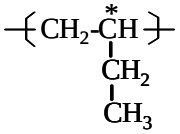
Researchers at Standard Oil of Indiana (now BP Amoco) and Phillips Petroleum (now Conoco Phillips) were also trying to synthesize polypropylene. In the end, this would lead to long complex legal suits. Pino and Moretti [40] indicated that D. R. Carmody in Standard Oil of Indiana may have synthesized isotactic polypropylene as early as 1950

but only characterized the product with infrared spectroscopy. However, knowledge of infrared spectroscopy at that time was insufficient to describe tacticity.

Phillips Petroleum [25, 26] also sought to polymerize propylene monomer. According to Pino and Moretti [40], E. Francis may have made isotactic polypropylene as early as 1951. Like Standard Oil of Indiana, Phillips Petroleum only characterized their new polypropylene with infrared spectroscopy and did not elucidate what it was. Synthesis of polypropylene is described in the first Hogan and Banks patent [25] filed in January 1953. Little is said of the characteristics of the polypropylene in the patent, and nothing is said of stereoregularity.

1.4 Isotactic Polybutene-1

Natta et al. [35–37] investigated the polymerization of 1-butene in the same period as their studies of polypropylene. They succeeded in producing isotactic polybutene-1, that is



(1-IV)

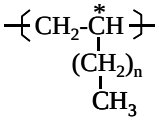
in 1954 and determined its crystal structure to prove its stereoregularity. It was characterized by peculiar polymorphic characteristics in which it would initially crystallize into one form (Form II) and then, within hours, recrystallize into a second form (Form I).

The polymerization of polybutene-1 is also described in the Hogan and Banks patent [25]. Little detail about its characteristics is given.

Petrotex Corp. began commercial development of isotactic polybutene-1 in 1963 with a 2000 lbs/day semiworks plant [26]. It was operated until 1966 and then abandoned as unpromising. In 1967, Mobil Corp. started up a plant in Texas with a capacity of 4 million lbs per year. In 1972, Mobil decided not to continue and licensed its technology to Witco Chemical. Witco then built a plant in Louisiana 50 with a capacity of million lbs per year. In 1977, the plant was sold to Shell [26]. Today this plant is operated by Basell.

1.5 Isotactic Polymers of Higher Olefins and Poly(4-Methyl Pentene-1)

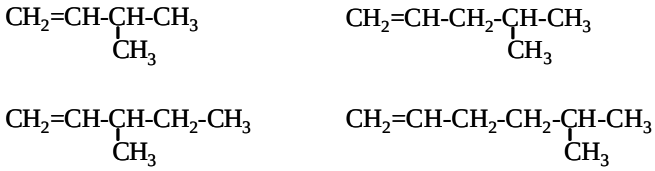
Natta et al. [37] followed up the polymerization of isotactic polypropylene and isotactic polybutene-1 with the synthesis of higher isotactic α-polyolefins. The polymers synthesized and their crystalline melting temperatures are listed in Table 1.1 [41]. These possess the structural unit



(1-V)

which contains an asymmetric carbon atom in each repeat unit. As n (the number of CH_2 units in the pending substituent) increases, the crystalline melting temperature decreases from 165 °C ($n = 0$) to 125 °C for $n = 1$, to 70 °C for $n = 2$ and to –55 °C for $n = 3$. Table 1.1 summarizes crystalline melting temperatures for this series which indicate that this was not a promising direction.

Natta and his coworkers now looked at branched polyolefins to achieve higher melting temperatures [37]. The monomers considered include



(1-VI)

Table 1.1 Melting Temperatures of Polyethylene and Isotactic Polymers of α-Olefins [41]

Polymer	T_m (°C)
Polyethylene	135
Polypropylene	165
Polybutene-1	128
Polypentene-1	70
Polyhexene-1	–55
Polyheptene-1	–40
Polyoctene-1	–38
Polydodecene-1	45
Polyoctadecene-1	70

The melting temperatures of isotactic polymers of all these monomers are higher than the one of isotactic polypropylene. The melting temperature of poly(3-methyl butene-1) was too high for it to be successfully processed. Poly(4-methyl pentene-1) had a melting temperature of about 235 °C and attracted the most attention. The polymer was also remarkable for its transparency, because the crystalline density was close to its amorphous density. However, it has a β-transition or glass transition of about 16 °C. This leads to problems with mechanical behavior at room temperature.

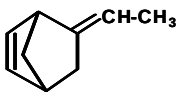
It should be noted that poly(4-methyl pentene-1) was also synthesized by Hogan and Banks in their patents, but little was said of its characteristics.

ICI started the commercial development of poly(4-methyl pentene-1) in 1965, and a plant with a capacity of 4.5 million lbs/year was built in 1968. Various papers on its characteristics were published [42–44]. ICI later licensed the technology to Mitsui Petrochemical, which has been its primary manufacturer since 1975. Phillips Petroleum manufactured this polymer for a short time in the 1990s.

1.6 Ethylene-Propylene Rubber

Early patents such as Zletz [23] and Hogan and Banks [25] discuss copolymerization of ethylene with other olefinic monomers such as propylene. However, the products are not discussed as materials. A 1955 patent application [45] by Natta with G. Mazzanti and G. Buschi describes the synthesis of elastomeric copolymers of ethylene with propylene, butene-1, pentene-1, and hexene-1. Typical polymerization initiators were aluminum trialkyl with $VOCl_3$. The patent was assigned to Montecatini.

Ethylene-propylene rubber was commercially produced in the late 1950s. The weakness of this product was that it could not be vulcanized. This was resolved by introducing a third monomer with two double bonds of unequal reactivity. Here, the more reactive double bonds are incorporated in the polymerization. The second double bond is used for vulcanization. The two major monomers that came to be used in small amounts with ethylene and propylene were



ethylidene norbornene

CH_2=CH-CH_2-CH=CH-CH_3

1,4-hexadiene

(1-VII)

Major manufacturers of ethylene-propylene terpolymers today include DuPont-Dow, Exxon Mobil, and Uniroyal Chemical.

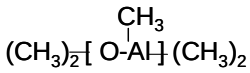
1.7 Metallocene Polymerization

Since Ziegler's announcement of polyethylene, chemists and industrial firms around the world sought to modify and improve his polymerization initiator system. Simmonazzi and Giannini [38] and Albizzati et al. [39] described the Montecatini-Himont efforts to improve Ziegler-Natta catalyst/initiator systems. The latter authors suggested that there have been six generations of catalysts related to isotactic polypropylene.

By the late 1970s, attention turned to systems such as [46]:

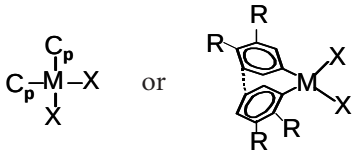
$$AlR_2Cl\ TiC_{p2}Cl_2 \tag{1-VIII}$$

where R is an alkyl group, and C_p is cyclopentadiene. Addition of water to the aluminum alkyl co-initiator converted it to complex aluminoxanes, which increased the catalyst activity substantially. If aluminum trimethyl is used, methyl aluminoxane, which has the following structure



(1-IX)

is formed. This has an especially high reactivity. Typical metallocene initiators involve it in combination with structures such as



(1-X)

where X is Cl or halogen, and R is H or alkyl. The metal M is usually Zr, Ti or Hf. The dashed line represents an optional bridge.

The development of this catalyst system can be followed through the work beginning with Ziegler et al. [21] to Natta et al. [34], Breslow and Newburg [47], Sinn et al. [48],

Ewen [49], and Kaminsky et al. [50]. Albizzatti et al. [39] call the metallocene catalysts '6th generation' stereospecific catalysts.

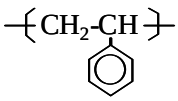
The metallocene catalysts proved able to produce highly stereoregular syndiotactic polyolefins. They have also been able to produce polyolefins with specific microstructure levels. The polymers synthesized had narrow molecular weight distributions.

These polymerization initiators have been developed by Dow Chemical, Exxon (later Exxon Mobil), Idemitsu Kosan, and others to develop new families of polyolefins and copolymers.

1.8 Stereoregular Polystyrenes

1.8.1 Isotactic Polystyrene

Atactic polystyrene, that is



(1-XI)

has long been known. It is an amorphous thermoplastic with a glass transition temperature of approx. 100 °C. It was first commercialized in the 1930s by the I. G. Farbenindustrie.

Isotactic polystyrene was one of the first polymers synthesized by Natta and his coworkers [51] in 1954–1955. It had a crystalline melting temperature of approx. 230 °C and was investigated by various industrial firms from the 1950s to the 1970s, but none decided to commercialize it. A major reason often cited was its slow crystallization rate.

1.8.2 Syndiotactic Polystyrene

Syndiotactic polystyrene was developed by Ishihara and his coworkers [52, 53] with Idemitsu Kosan in the mid 1980s using metallocene initiators. It has a crystalline melting temperature of approx. 270 °C. The material is being commercially developed by Idemitsu and Dow Chemical.

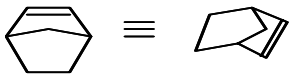
1.9 Syndiotactic Polypropylene

Syndiotactic polypropylene is another stereoregular form of polypropylene. It has a crystalline melting temperature of approx. 155 °C (in highly stereoregular polymers). The synthesis of syndiotactic polypropylene was first reported by Natta and his coworkers [54, 55] in 1960–1962.

The early-stage syndiotactic polypropylenes produced using vanadium-based Ziegler-Natta catalysts contained significant amounts of isotactic segment blocks and stereo-irregularities. This led to low syndiotacticity levels (usually 60 to 70% syndiotactic tetrads) and poor mechanical and thermal properties. In more recent years, new metallocene catalysts allowed major improvements in syndiotactic polypropylene. It became commercially available in the 1990s. Fina Oil and its successor AtoFina Petrochemicals brought syndiotactic polypropylene to the market place.

1.10 Cyclopolyolefins

The polymerization of norbornene



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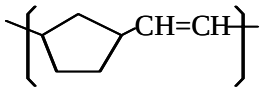
was first described in the late 1950s by DuPont researchers [56–58]. They used a Ziegler-type lithium aluminum trialkyl-titanium tetrachloride catalyst. The polymer synthesized had the structure



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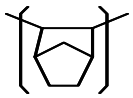
In March 1964, a patent application by McKeon and Starcher [59] of Union Carbide described the polymerization of norbornene with palladium compounds leading to the structural unit



(1-XIV)