Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Vogl, Otto(1998) 'Polyolefins: Syntheses and Structures', Journal of Macromolecular Science, Part A, 35: 7, 1017 — 1035
To link to this Article: DOI: 10.1080/10601329808002097
URL: http://dx.doi.org/10.1080/10601329808002097

J.M.S.—PURE APPL. CHEM., A35(7&8), pp. 1017–1035 (1998)

POLYOLEFINS: SYNTHESES AND STRUCTURES

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Key Words: Polyolefins, Polyethylene, Polypropylene, Crystallization, Right-handed, Left-handed Helix, Rigid Helix, Chiral Nucleation

ABSTRACT

Commodity plastics, especially polyolefins are the most important group of plastic materials. Polyethylenes constitute about 60% of polyolefins and will reach a capacity of about 60 million tons a year by the year 2000. New initiating systems are now being developed for an even more efficient production of polyolefins. For substituted polyolefins, like polypropylene, novel technology will allow the control of stereospecificity of the polymer products, and more importantly, will allow us to control molecular weights and molecular weight distributions. These developments will allow for the control of morphological engineering of polyolefin properties by controlling, among other things, the nucleation of polymer crystallization.

INTRODUCTION

Polymer science and technology and the industrial production of plastics materials have made spectacular progress in the last 50 years (1-4) (Figure 1). Approximately 180 million tons of polymers are annually produced world-wide.

Over 20 years ago, when the plastics production and use had reached 60 million tons, it was predicted that the plastics used would reach 200 million tons

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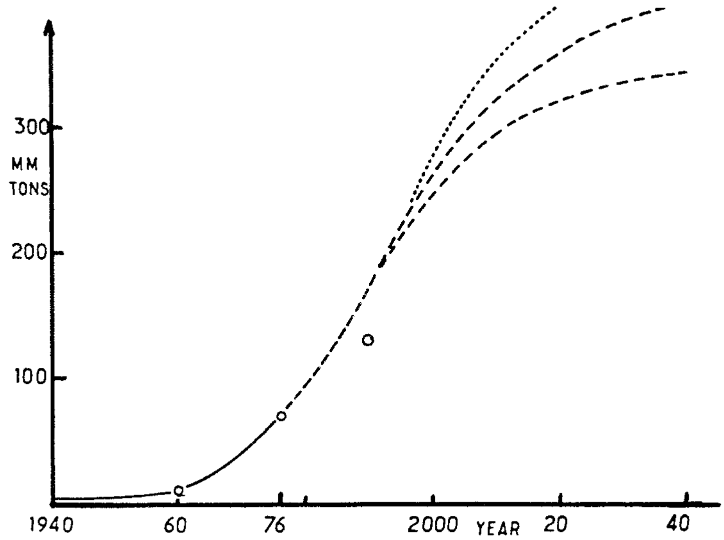


Figure 1. Prediction of world-wide polymer production in 1976.

per year by the year 2000 (Figure 2) [3, 5]. The projected tonnage that had been expected were not quite reached in the decade of the 1980's. World-wide economic slow-down following a recession in the industrialized countries and a slower rate of expansion in the developing countries seem to have been the reason for the slower plastics growth. A significant "up-turn" in the early 1990's, with an overall healthy growth rate, seems to make the goal of 200 million tons per year achievable by the year 2000.

Commodity Plastics

Most of the volume of plastics materials belong to the category of commodity plastics, materials that fulfill the every day needs of most applications at reasonable prices. These are the high volume, low cost materials of which 100 million tons are produced annually. They include polyethylene (PE), polypropylene (PP), polystyrene (PSt), and poly(vinyl chloride) (PVC) [6] (Figure 3). All these polymers are made from monomers that had been made from the 3.8 billion tons of crude oil that are harvested annually. The plastics industry does not even use 4% of our crude oil.

Over 40% of the commodity plastics are the polyethylenes, low density PE, (LDPE), high density PE (HDPE) and the now separately registered category, called linear low density (LLDPE). LDPE is prepared by radical polymerization of

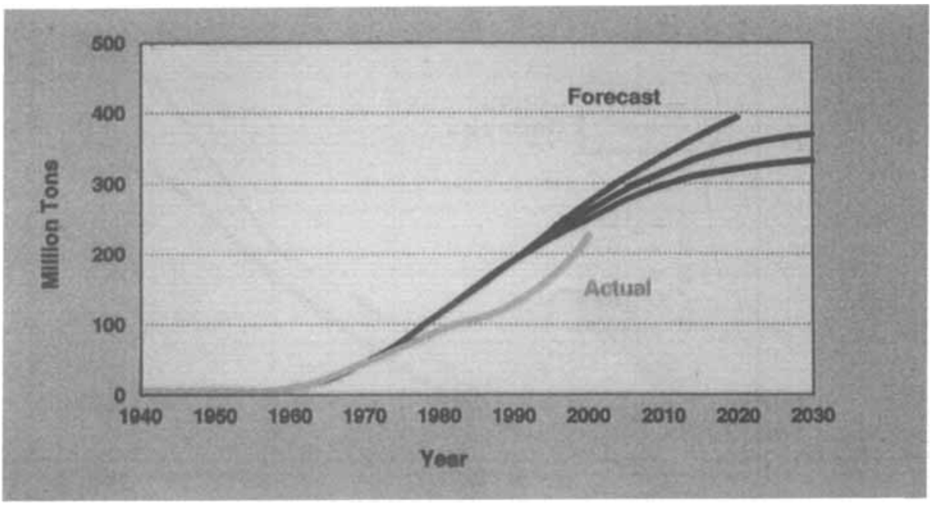


Figure 2. Worldwide polymer production since 1940.

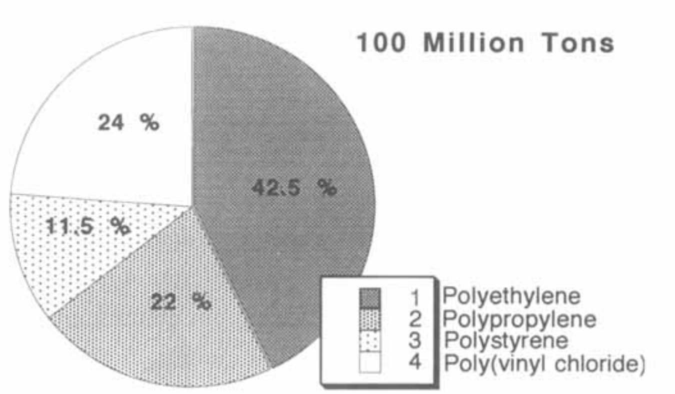


Figure 3. Commodity plastics use in 1996 (after Ref. 6).

ethylene under high pressure while the other PE's are produced by coordination polymerization using transition metal initiating systems. All polyolefins are made from monomers, such as ethylene, propylene and butadiene, that are produced by proper cracking procedures from crude oil.

Production and use of commodity plastics has more than doubled in the last decade. The growth of PP is most startling and has proceeded with an overall growth rate of 20% for some time [7].

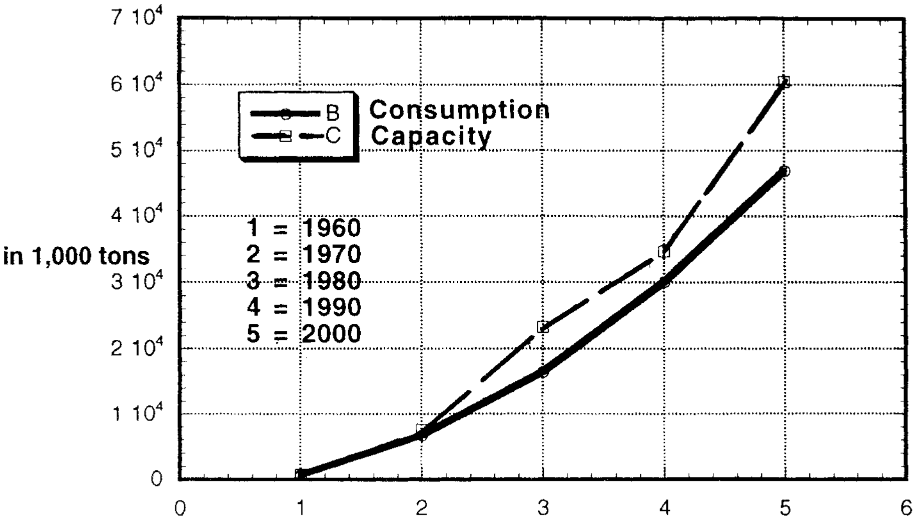


Figure 4. Polyethylene development in the last 40 years.

Polyethylene

First of all, I would like to discuss some basic principles of the development and growth of PE. Figure 5 compares the development of plant capacity and polymer consumption of PE over the last 4 decades [8]. By the year 2000, we expect to produce about 60 million tons of the various types of PE and the consumption will reach about 48 million tons (Figure 4). Since 1990, the PE capacity grew at a rate of about 7.5%; for 1997, a 7% growth rate is projected; for the year 2000 the growth rate is predicted to slow down to 3.6% (Figure 5).

The fastest growing type of PE is LLDPE with a growth rate of about 12% in the last 10 years, as can be seen from the Figures. The production of LLDPE passed that of LDPE in 1995 and will pass that of HDPE before the year of 2000 (Figure 6).

The projected world wide distribution of the capacity of PE production and consumption in 2000 is shown in Figure 7. It shows that the USA (North America) will continue to lead in these areas, while Western Europe and Asia will gain in the capacity of PE production. In Japan, the production of PE increased at a moderate rate of 2.5%, and the overall plastics production of about 4%, with PP being the largest gainer with a rate of about 8.5%. Korea, on the other hand, has a 4 year plastics growth rate of about 10 to 15%. China is producing only 5 million tons of plastics materials at this time at a growth rate of about 12%, but China is a

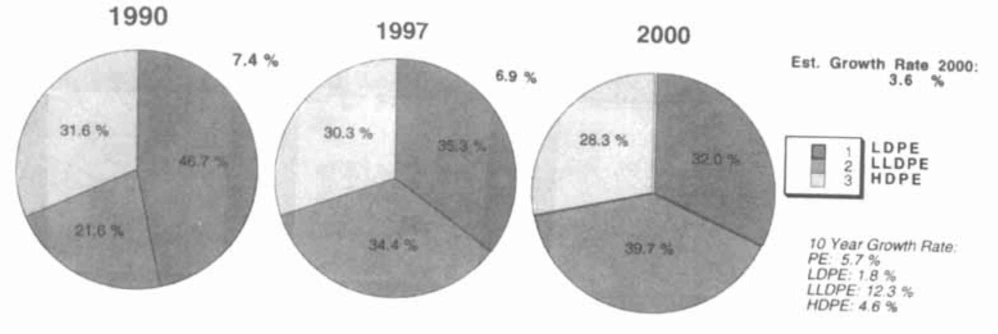


Figure 5. Worldwide polyethylene capacity development in the last decade.

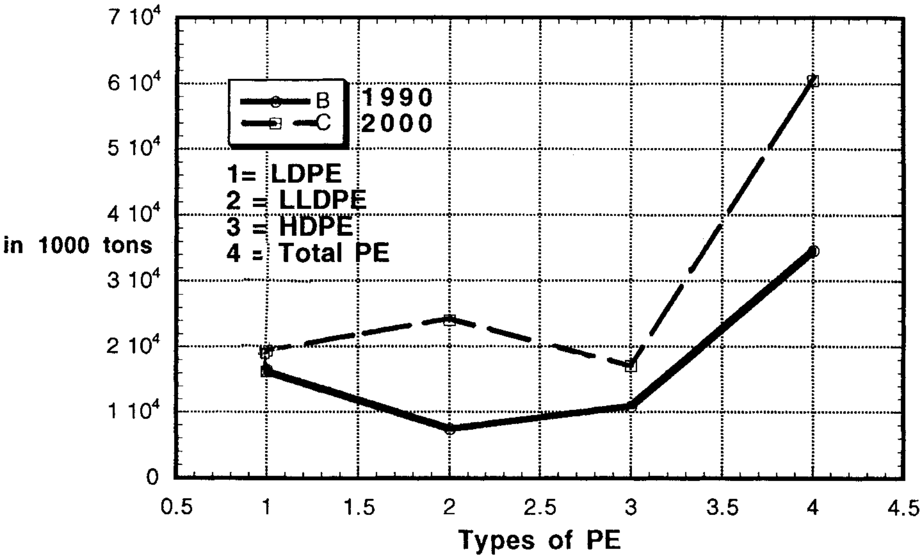


Figure 6. Polyethylene capacity according to types (after Ref. 8).

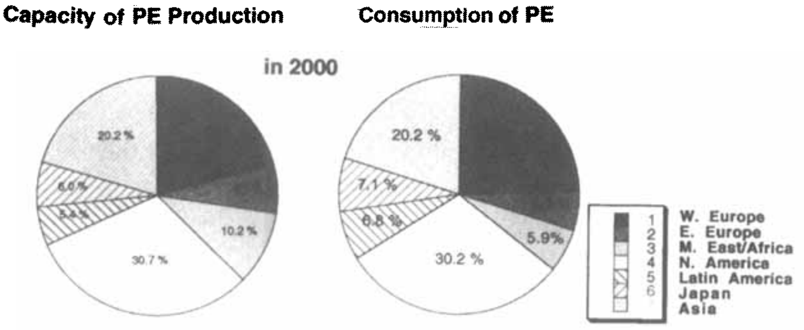


Figure 7. Projected worldwide: a.) capacity of polyethylene production; b.) consumption of polyethylene (after Ref. 8).

		10^3 Tons	4 Year Growth Rate
Japan:	PE 96:	3,300	~2.5 %
	PP 96:	2,700	~8.5 %
	Plastics:	12,500	~4 %
Korea:	PE 96:	2,640	~11.5 %
	PP 96:	1,740	~10.5 %
	Plastics:		~15 %
China:	Plastics:	4,900	~12 %
Taiwan:	Plastics:	6,500	~8.5 %
U.S:	Plastics:		~5.5 %
France	PE 96:	3,380	~3.5 %
	PP 96:	2,500	~6 %
Germany:	PE 96:	2,025	~2 %
	PP 96:	1,100	negative
Italy:	PE 96:	2,300	~3.5 %

Figure 8. World-wide production of polyolefins according to region.

substantial importer of plastics, consequently, the actual consumption is higher. Taiwan is producing 6.5 million tons of plastics with a growth rate of about 8.5% (Figure 8).

The production of PE and PP in the European countries ranges from 1 to 3 million tons each, depending on the country, with rather modest growth rates of 2 to 4%. The UK shows a substantially larger growth rate, however, this is a reflection of the recent extensive increase in the plant capacities in the UK. In Europe, one third of PE is produced by the high pressure free radical process and two thirds by coordination polymerization. Of the polyolefins, PP has had the most spectacular growth, on the average twice that of PE, and has now 25% of the commodity plastics market. PP is produced basically by three processes: by the old process in hexane suspension, by the bulk process in liquid PP; and some PP is also produced by gas phase processes (Figure 9).

Polyolefin Processes

Now, a few comments on the production of polyolefins. While some preparation of PE can be traced to the late 19th century, these PE samples were never

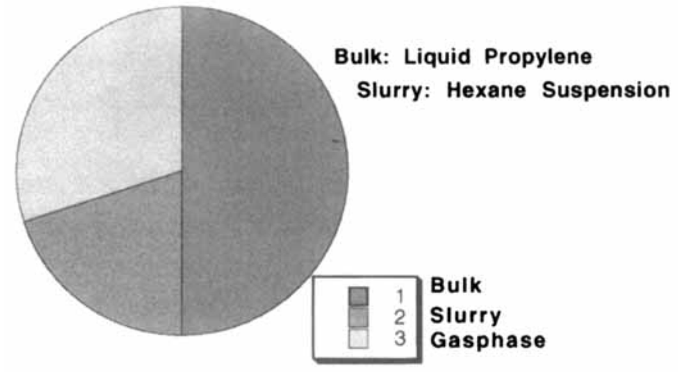


Figure 9. Processes of polypropylene production.

recognized or properly characterized. In 1934, PE was first prepared in England during studies of chemical reactions under high pressure [9]. The major breakthrough was the technical development of steel for high pressure reactors that could contain reactions and maintain these reactions under thousands of atmospheres of pressure and elevated temperatures. Because of many technical difficulties and circum-stances, particularly during the second World War, the PE production did not start seriously and on a large scale until the early 1950's. The early reactors were vessel reactors, now the high pressure polymerization of ethylene is more frequently, if not exclusively, carried out in tubular reactors.

The new era of olefin polymerization was initiated in 1953, when it was found that transition metal initiating systems, both in solution and in the solid state, could produce first PE [10] and then PP]11], the latter process became commercial in 1957. The systems that produced high molecular weight PE included chromium and molybdenum compounds on carriers or reaction products of titanium tetrachloride and triethylaluminum, the so-called Ziegler-Natta type catalyst systems. [12].

It is from the latter systems that research, development, and production of PE, but also of PP, proceeded explosively and produced the technology that we have today for the various kinds of olefin polymers.

Polypropylene

For the polymerization of propylene, it was soon found that not titanium tetrachloride, but titanium trichloride with diethylaluminumchloride as the reducing agent and with various activators became essential for the production of PP.

These initiating systems produce catalysts that have about 3% of active transition metal sites. Most of the activity of the transition metal ions are lost because they agglomerate and cluster and are consequently lost for the catalyst activity of the olefin polymerization.

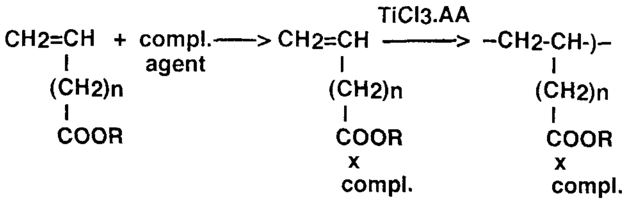
Extensive investigations, to a great degree by trial and error, showed that magnesium chloride has the unusual capability of separating metal ions by forming solid solutions with many transition metal ions and these systems produced initiating systems (together with the reducing agents), that utilize 70% and more of the transition metal ions as catalytic sites and are called "high yield catalysts" [13, 14]. Now, only 2 to 3 parts per million of transition metal ions are used for the olefin polymerization and the transition metal ions can be left in the polymer, and have no detrimental effect on polymer stability. These systems have some slight disadvantage because, from the magnesium chloride carrier, a relatively high amount of chloride (20 to 30 ppm) is left in the polymer which causes some corrosion on the processing equipment during high temperature melt processing.

In the first years of studies on coordination, polymerization of olefins attempts had been made to polymerize ethylene with transition metal catalysts but without additional reducing agents, i.e. aluminum alkyls. During these investigations, it had been found that dicyclopentadienyl titanium dichloride had some activity for the polymerization of ethylene [15]. This discovery was the beginning of the development of what we now call metallocene initiating systems.

Over the years, more and more efficient initiating systems for olefin polymerization based on transition metals were invented and became the center of commercial processes such as the Unipol process for PE [16] and the Spheripol process for PP [13]. These processes allowed the preparation of the polyolefins without the removal of the transition metal and even in the shape and bulk density that allows direct melt processing of the polyolefin.

The polymerization of olefins with functional groups had been the focus of some considerable interest. It was finally found the precomplexation of the functional group was essential while using flexible methylene spacer groups to separate the functional (complexed) ester group from the polymerizable terminal vinyl group [17, 18] (Figure 10). Under these conditions regular PP polymerization initiators could be used.

A further development in propylene polymerization was the discovery of elastomeric PP in 1980 [19, 20]. For this polymerization, zirconium complexes, rather then titanium compounds were preferably used. Elastomeric PP can take



$$\underset{\substack{|\\ (CH_2)_n\\ |\\ COOR}}{CH_2{=}CH} + \underset{agent}{compl.} \longrightarrow \underset{\substack{|\\ (CH_2)_n\\ |\\ COOR\\ x\\ compl.}}{CH_2{=}CH} \xrightarrow{TiCl_3.AA} \underset{\substack{|\\ (CH_2)_n\\ |\\ COOR\\ x\\ compl.}}{-CH_2{-}CH{-})-}$$

Figure 10. Polymerization of functional polyolefins.

various forms. It was originally described as a ABA triblock polymer of isotactic-atactic and isotactic PP of specific sequence length. Today, it could be a multi-block polymer of isotactic and atactic PP blocks, with isotactic blocks long enough to crystallize.

Unusual Polyolefins

Over 20 years ago, some interest arose to synthesize and study the properties of unusual structures of commodity plastics, especially those of polyolefins. The focus centered on the preparation of head-to-head (H-H) polymers. Regular addition polymers have head-to-tail (H-T) structures. It was our objective to develop an understanding of the basic properties of H-H polymers, to study their spectroscopic thermal and blending behavior, and compare these properties with the regular H-T polymers. In addition to the investigation on H-H PSt, H-H PP and H-H polyisobutylene were synthesized and studied. H-H PP has a T_g of -39°C, and is made by hydrogenation of the 1,4-polymer of 2,3-dimethylbutadiene. Nearly pure erythro and threo H-H PP's were synthesized and it was found that H-H PP at 50:50 mixtures are miscible (T_g = -28°C) with atactic H-T PP of a T_g = -17°C of comparable molecular weight [21, 22]. H-H polyisobutylene [23] is not miscible over almost the entire composition range with H-T polyisobutylene [24, 25].

New Developments in Olefin Polymerization

The 1980's brought the recognition that metallocenes, transition metal complexes with bis-indanyl ligands [26] provide unique opportunities to tailor-make initiating systems for olefin polymerization. Metallocene initiators allowed the increase of the isotacticity of the polymers, the "livingness" of the polymerization, and at the same time increase the rate of polymerization and to prepare syndiotactic polymers. Originally, zirconium was the transition metal of choice

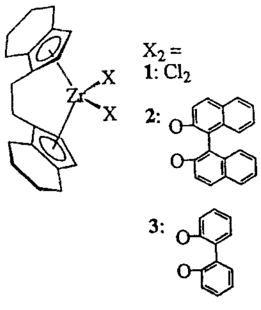


Figure 11. Typical structures of metallocenes.

with some of the ligands connected by the proper spacer groups [27]. An example is shown in Figure 11.

It became clear that the valancy of the transition metal and the coordination number of the central transition metal as well as the ligand structure together with the monomer to be polymerized, provide the right "stability/instability" for the initiating system to be effective for polymerization. Most of the metallocenes are only suitable for the polymerization of saturated olefins. Newer studies have shown that polymerization systems are now available that allow the copolymerization of ethylene and styrene [28] and for the efficient polymerization of propylene to syndiotactic PP [29, 30] and styrene to syndiotactic PSt [31].

It was mentioned earlier that the use especially for copolymerization of olefins with ester functionality, was a desirable goal. With metallocene catalysts, it is possible to incorporate norbornene type carboxylates into polyolefins. As we go from coordination numbers 6 to 8, more flexibility of the initiating systems are noticed. If we go to even larger central atoms with coordination numbers as high as 12, the lanthanides, additional functional monomers, became polymerizable (Figure 12). With metallocenes of samarium and yttrium as the central atoms of the complexes, even acrylates and methacrylates can be polymerized to polymers of high molecular weight and with reasonable narrow molecular weight distribution [32]. Even block copolymers of ethylene and acrylates have been claimed to have been prepared.

In order to avoid the problems associated with the magnesium chloride in high yield catalysts, other chloride-free systems have been investigated. It had been known for a long time that trialkylaluminum and other alkylaluminum compounds could be carefully hydrolyzed, either with water alone or better in combi-

$SmH(C_5Me_5)_3$

$SmMe(C_5Me_5)_2(THF)_2$

$YMe(C_5Me_5)_2(THF)_2$

(Meth)acrylates
Lactones

Not Stereospecific for (Meth)acrylates but of
Living Nature for (Meth)acrylates and Lactones

Figure 12. Typical structures of rare earth initiators.

nation with other compounds to give excellent catalyst systems for the polymerization of epoxides and lactones [33, 34]. These aluminoxane systems were not used as reducing agents for Ziegler-Natta type catalysts at that time. It was found that the controlled hydrolysis of trimethylaluminum produces methyl-aluminoxane which is much more effective, as the methyl group seems to be a much better alkylating agent for the transition metal in the transition metal complex [35], and gives catalyst systems that are chloride-free. One disadvantage seems to be that relatively large amounts of methyl-aluminoxane have to be used.

For many years, the objective in ethylene polymerization was to produce the polymer faster at a predetermined molecular weight and molecular weight distribution, to control, design or to eliminate chain branching. These needs were pursued with the transition metals known from Ziegler-Natta type of metallocene catalysts, catalysts based on group VIII metals which have occasionally been investigated, in attempts to polymerize functional olefins. It was recently found that a new type of polyethylene could be produced using nickel, palladium coordination compounds as exemplified in Figure 13 [36]. These ethylene polymers are highly branched structures of high molecular weight and are produced at a good rate of polymerization. Not only can ethylene be polymerized, but it can also be copolymerized with α-olefins and give copolymers of peculiar structure, in which the comonomer might be incorporated α,ω and proceeds by extensive 1,2-hydride transfer to allow the carbocation to move along the polymer chain. It seems that this type of polymerization and copolymerization is a coordinative cationic polymerization, while the regular coordination polymerization of olefins is a coordinative anionic polymerization.

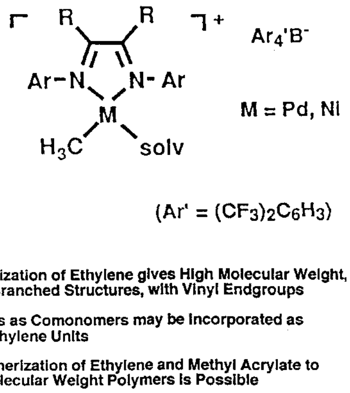


Figure 13. Polymerization with Ni(II) and Pd(II) based initiating systems.

Although other poly(α-olefins) have also been studied extensively, only the polymers of butene-1 and 2-methylpentene-1 are actually commercially produced. These polymers are low volume specialty materials that have never reached the importance approaching that of PP.

Polypropylene Crystallization

Many of the mechanical and physical properties of PP depend on the chemical fine structure which influences the basic structure of PP in the solid state. PP is a semi-crystalline polymer, its solid-state structure is determined by molecular weight, molecular weight distribution, stereoregular purity, i.e. degree of tacticity, nucleation and rate of crystallization. Isotactic PP is a 3_1 helix with a repeat distance of the c-axis of 6.6 Å. The helix is capable of chain folding and the folded chain lamellae are then incorporated into spherulites. PP is a semi-crystalline polymer with a crystallinity of 40-60% and a T_m of about 165°C [36].

Closer investigation showed that the crystal structure of PP consisted of three phases: the α-phase, the β-phase and the γ-phase. The helical structure of PP is arranged as 50:50 mixtures of left-handed and right-handed helices [36]. They are produced by allowing statistical nucleation to occur and the 50:50 mixtures of left- and right-handed helices are formed because there is an equal opportunity to form *either* a left-handed or a right-handed nucleus.

The different phases of PP have the same 3_1 helical conformation but the arrangements of the left- and right-handed helices are slightly different. The α-phase has a T_m of about 170°C and the β-phase of 155°C. Several differing T_m

3 Crystal Modifications: c-Axis: 6.5 Å

α-Phase: Monoclinic Tm: 170°C

β-Phase: Hexagonal Tm: 155°C

γ-Phase: Triclinic Tm: 125-150°C,
173°C
(Phase Centered Orthorhombic)

Figure 14. Structures of isotactic polypropylene.

values have been reported for the γ-phase. In normally crystallized PP, the α- and the γ-phases coexist. The γ-phase crystallizes in the branching points of the spherulitic structure of the α-phase. It has been reported that the α-phase crystallizes faster above 140°C, and below 105°C, the γ-phase has a faster rate of crystallization between 105°C and 140°C. Depending of the details of PP crystallization, the γ-phase is incorporated in the α-phase in various degrees (Figure 14).

The structure of the α-phase was already determined in 1960 by Corradini [37]. The left- and right-handed helices had to be arranged in a monoclinic arrangement. The γ-phase was only recently worked out [38, 39]. For structure determination by X-rays, a fiber diagram has to be produced, but the γ-phase reverted to the α-phase on stretching. Modern X-ray structure determination techniques, together with modeling, established the correct structure. The β-phase [40] has to be specially nucleated and is not found in semi-crystalline PP, crystallized by spontaneous crystallization. The traditional way of determining crystal structures of polymers is by analyzing the fiber diagram.

Recently, atomic force spectroscopy in combination with computer modeling, was found to be useful for the establishing the crystal structures of polymers. By this approach, the structure of syndiotactic PP was shown to have *ttgg* conformation of the racemo-structure of the syndiotactic PP chain.

Isotactic polyolefins, such as PP, normally crystallize in a 3_1 helix. As the bulk size of the substituent in the monomer increases from the methyl group in propylene to larger groups, the polymerization of those monomers gives more readily stereoregular, isotactic, polymer structures [41]. Ethylenes, substituted with 2-isopropyl- groups (3-methylbutene-1) and 2-n-butyl-groups (n-hexene-1), give

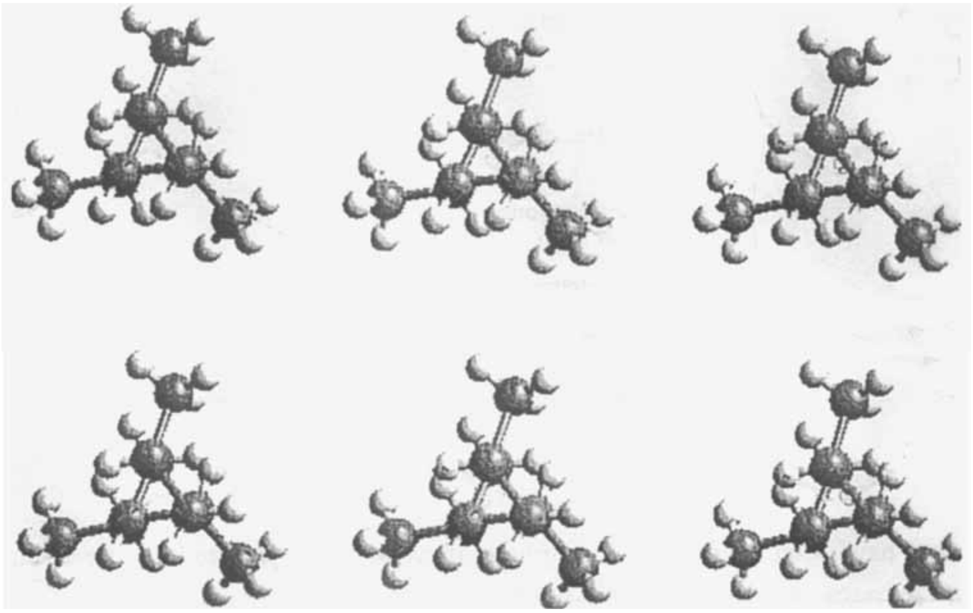


Figure 15. Computer model of a possible structure of chiral isotactic polypropylene.

much more readily isotactic polymers and those isotactic polyolefins crystallize in 7_2 helices; isotactic poly(cyclohexylethylene-1) crystallizes in a 4_1 helix.

One crystalline phase of PP has never been observed: isotactic chiral PP [42]. This structure would be different from the α-phase, the β-phase and the γ-phase of PP, and should exist of helices of one screw sense, either right- or left-handed, and should be accessible by chiral nucleation (Figure 15). PP has a rather flexible chain in the liquid state, melt or solution, and would readily be the subject of helix inversion. In principle, chiral PP could also be prepared by polymerization of PP with a chiral initiator, for example, a metallocene initiator, where the initiator site is chiral [43]. In this case, the polymer would be obtained as non-folded, chain-extended native polymer structure. However, on melting or dissolving the polymer, it would undergo helix inversion and end up as a 50:50 left- and right-handed helical polymer structure (Figure 16). The chirality in helical polymers singlehandedness of the helix) can result for various reasons as shown in Table 1.

As indicated, the helical structure of crystalline PP is a 3_1 polymer helix. If all hydrogen atoms in PP are replaced by fluorine atoms, the resulting polymer is polyhexafluoropropylene. It was prepared many years ago [44] by high pressure

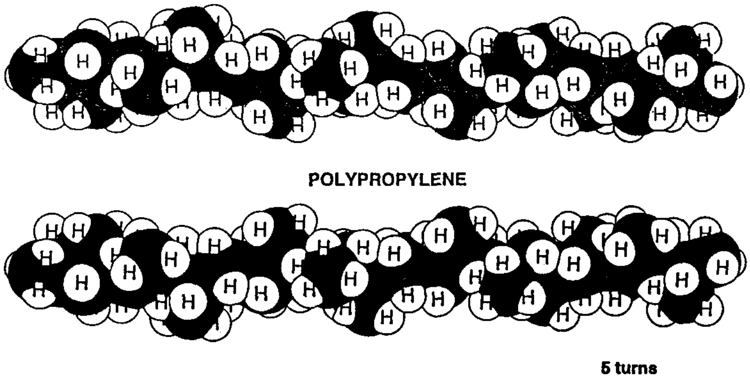


Figure 16. Spacefilling models of "racemic" polypropylene.

TABLE 1. Reason for One Handednessof a Polymer Helix

1. Chiral Center is in the Polymer Main Chain
2. Chiral Center is in the α-Position to the Polymer Chain
3. No True Chiral Center Exists in the Monomner Unit of the Polymer but Handedness is Introduced by Chiral Additive
5. Rigid Helix: Configurationally and Conformationally Specific Polymerization
6. Chiral Separation of Rigid Helical Polyers
7. Chiral Nucleation of Crystallization to Produce Helical Polymers in the Solid State, i.e Chiral Isotactic Polypropylene, but in Principle of all and every Helical Polymers, i.e.Chiral Polyformaldehyde and even Polypivalolactone.

polymerization. Recently, modeling of the most stable PHFP structure has been undertaken and it was found that PHFP is expected to have a slightly extended 3_1 helix, actually a 17_6 isotactic helix as the most stable configuration and conformation which requires 2.83 monomer units per turn, or a rotational angle of 127° [45] (Figure 17).

Other Helical Polymers

Stereoregular helical polymers of addition polymers, that are not based on the basic structure of polyethylene, are the substituted polyoxymethylenes. They

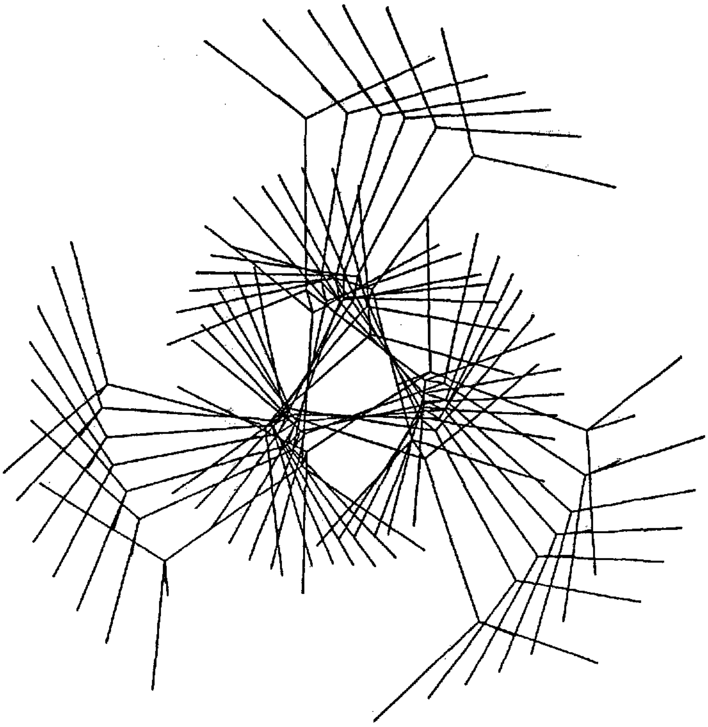


Figure 17. Stick model representation of molecular modeling of isotactic polyhexafluoropropylene: top view.

need to be mentioned here because they show the relationship of bulk size of the side group of the monomer unit on the helical conformation of the stereoregular polymer [46] (Figure 18).

Isotactic polyacetaldehyde has 3.91 monomer units in the repeat meaning, an almost 4_1 helix, while polytrifluoroacetaldehyde has 3.71 monomer units in the repeat which is close to a 11_3 helical conformation. Polyacetaldehyde and polyfluoral still show some flexibility of the polyoxymethylene backbone chain. In isotactic polyacetaldehyde, the bulk effect of the methyl group is the only effect that affects the helical conformation of the polymer in the solid state. In polytrifluoroacetaldehyde the conformation of the polymer helix is influenced by both steric and electronic effects, which produce the 11_3 helical conformation. Polychloral, and even more, polybromal, are completely rigid helices, and exist only in isotactic stereochemistry [47]. They have 3.7 monomer units in the repeat, which constitutes a 11_3 helical conformation. In these rigid structures of poly-chloral and

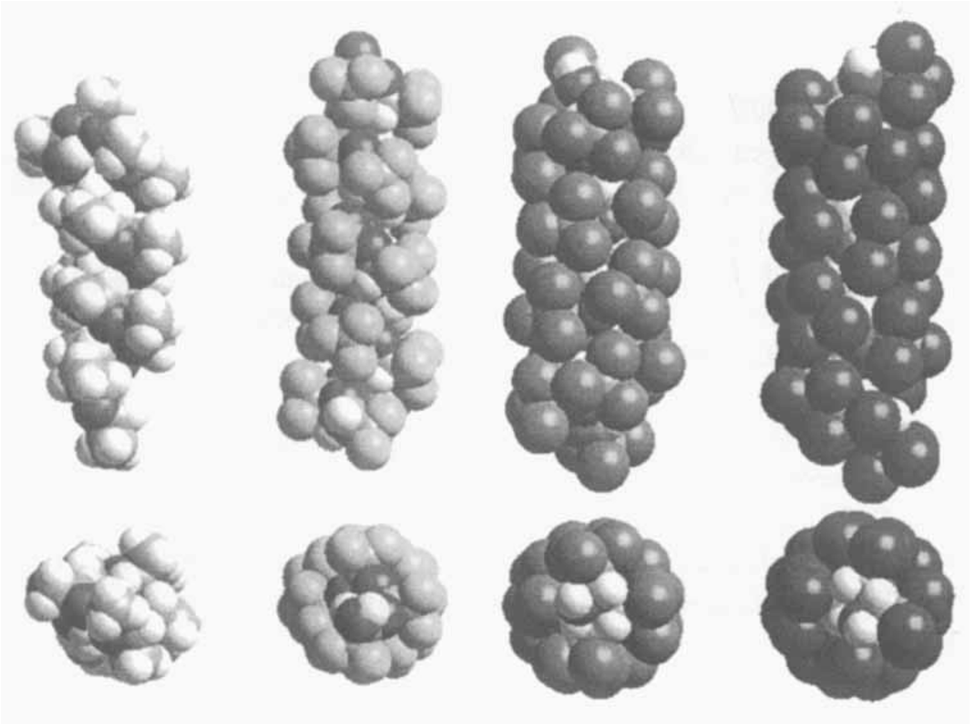


Figure 18. Computer created structures of isotactic polyaldehydes.

polybromal, the polymer structure, its stereochemistry, and conformational specificity, is formed directly during the polymerization process.

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