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Introduction to Polymers of Propylene

1.1 Origins of Crystalline Polypropylene

Crystalline polypropylene (PP*) was unknown to the world before the 1950s. Though oligomeric and polymeric forms of propylene had been made before that time, they were typically amorphous, low molecular weight oils [1]. These liquid/oily polymers were produced by polymerization or oligomerization of propylene using free radical initiators or acidic/cationic catalysts at high temperature and pressure and were of marginal commercial value.

Giulio Natta is widely regarded as the discoverer of crystalline polypropylene, resulting from an experiment Natta performed in his lab in Milan, Italy on March 11, 1954 [2]. Without question, Natta contributed mightily to the fundamental understanding of crystalline polypropylene and its stereochemistry and richly deserved the admiration accorded him. However, with respect to US patent rights, who first prepared crystalline polypropylene remained a litigious issue for many years. Ownership of the US patent rights for crystalline

* Please see glossary for definition of abbreviations, acronyms and terms.

2 INTRODUCTION TO INDUSTRIAL POLYPROPYLENE

polypropylene was resolved only after nearly three decades of legal wrangling (interferences, appeals and much rancorous debate). Testimony in the case resulted in about 14,000 pages of text and 4,600 exhibits [3]. Nuances of polypropylene discovery and patent rights are beyond the purview of this text, but the interested reader can find more information in references [1–4]. In the final analysis, the courts awarded priority to Phillips Petroleum Company, tacitly acknowledging that Phillips chemists J. Paul Hogan and Robert L. Banks had first prepared crystalline polypropylene in an experiment conducted on June 5, 1951. On March 15, 1983, some 30 years after the original application, a definitive patent was finally issued to Hogan and Banks and rights assigned to Phillips covering solid polypropylene “having a substantial crystalline polypropylene content” [5].

In their discovery experiment, Hogan and Banks used a chromia-NiO catalyst supported on silica-alumina. Later, they demonstrated that it was the chromium portion of the catalyst that was responsible for polymerizing propylene to the crystalline polymer. Hogan and Banks were belatedly honored for their contributions to polyolefin technology with several awards, including the 1987 Perkin Medal by the Society of Chemical Industry. Hogan and Banks were also inducted into the National Inventors Hall of Fame in 2001 and the building in Bartlesville, Oklahoma in which they made their seminal discoveries on polyolefins was designated an “historic landmark” by the American Chemical Society [6]. Ironically, while it is true that the Phillips catalyst is today enormously important in manufacture of polyethylene (accounting for approximately a quarter of all polyethylene produced globally), it is unsatisfactory for commercial production of polypropylene [7].

In March of 1954, nearly 3 years after the Hogan-Banks discovery experiment, Natta synthesized crystalline polypropylene using a transition metal catalyst (and a metal alkyl cocatalyst) of the type that emerged from the remarkably fruitful work of Karl Ziegler in polyethylene. In recognition of the pioneering work of Karl Ziegler and Giulio Natta, polyolefin catalysts involving combinations of transition metal compounds with metal alkyl cocatalysts have become known as Ziegler-Natta catalysts [8]. Today, the vast majority (>97%) of industrial polypropylene as well as huge quantities of polyethylene are produced with modern versions of Ziegler-Natta catalysts. Ziegler and Natta shared the Nobel Prize in chemistry in 1963. A timeline of 20th century milestones in polypropylene is provided in Figure 1.1. More information on the origins and evolution of stereoregular polypropylene and Ziegler-Natta catalysts will be provided in Chapters 3 and 4.

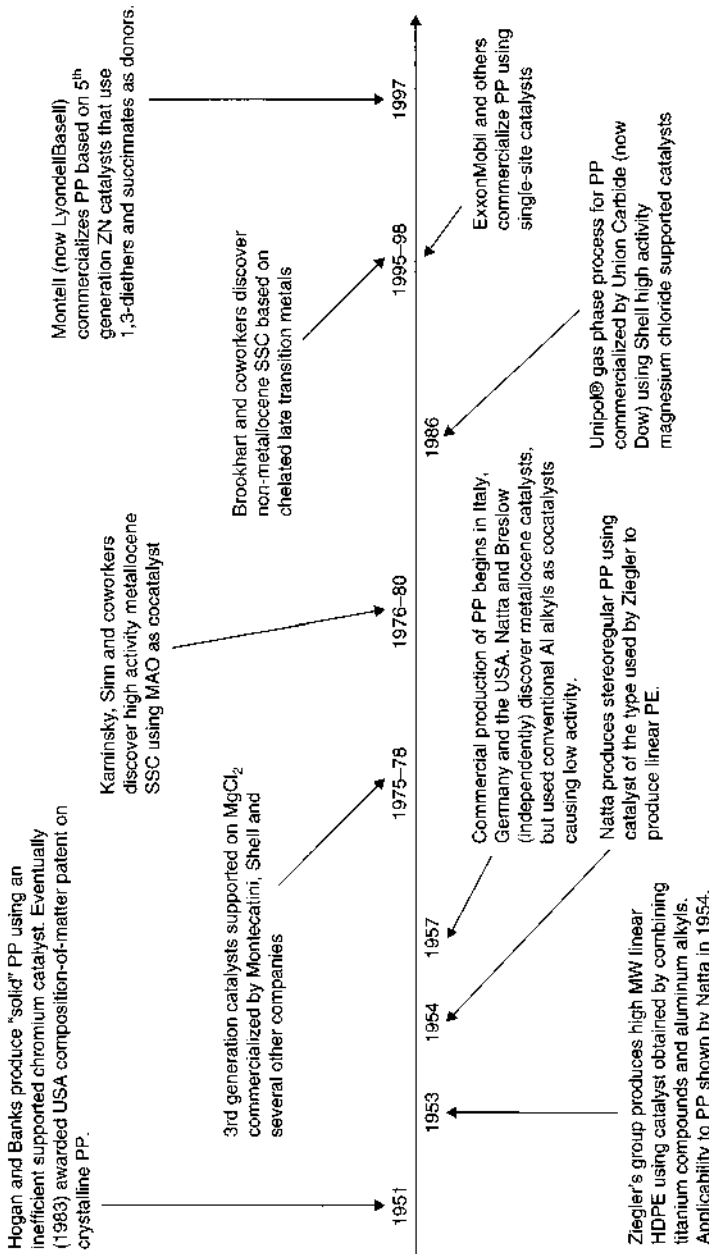
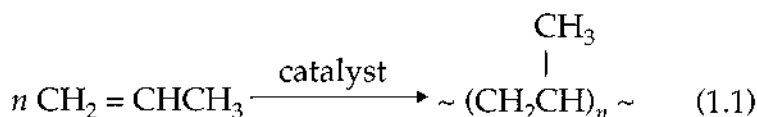


Figure 1.1 20th century milestones in polypropylene.

1.2 Basic Description of Polypropylene

Propylene (aka propene) has molecular formula C_3H_6 . Other than ethylene, it is the simplest alkene, but in the parlance of the polypropylene industry is more commonly called an olefin. Propylene may be polymerized through the action of catalysts (eq 1.1). To obtain satisfactory quantities of stereoregular polypropylene, polymerization must be conducted under proper conditions using a transition metal catalyst and a metal alkyl cocatalyst. Other catalysts (free radical, cationic, *etc.*) typically produce low molecular weight amorphous polypropylene that is of limited commercial value.



Note that the basic repeating unit of polypropylene contains a primary (1°), a secondary (2°) and a tertiary (3°) carbon atom. Note further that the tertiary carbon atom is chiral. Consequences of these characteristics will be developed in subsequent discussions. Ziegler-Natta catalysts are the most important transition metal catalysts for industrial polypropylene and titanium is, by far, the most widely used transition metal. We will introduce key aspects of Ziegler-Natta catalysts in section 1.5 below, and examine Ziegler-Natta catalysts in greater detail in Chapters 3 and 4.

Like Ziegler-Natta catalysts, single site catalysts (SSC) employ transition metal compounds and can be used to polymerize propylene. In the mid-1970s, Kaminsky and Sinn [9] found that SSC of extraordinarily high activity could be obtained if methylaluminumoxanes (rather than conventional aluminum alkyls) are used as cocatalysts. This discovery sparked a renaissance in polyolefin catalyst research and a surge in literature and patents touting the attributes of polymers made with SSC. Single site catalysts exhibit exceptional activity and permit unprecedented control over the molecular architecture of polymers (see Chapter 6). However, it is important to keep SSC in perspective relative to industrial polypropylene. As of this writing, the quantity of commercial polypropylene produced with single site catalysts is very small (<3%). As more cost-effective SSC are developed, the percentage of polypropylene made with SSC will undoubtedly grow in the coming years.

However, Ziegler-Natta catalysts will remain the dominant catalysts for industrial polypropylene well into the 21st century.

Conditions for polymerization vary widely and polypropylene compositions also differ substantially in structure and properties. In eq 1, subscript n is termed the degree of polymerization (DP) and is greater than 1000 for most of the commercially available grades of polypropylene. As removed from industrial-scale reactors under ambient conditions, stereoregular polypropylene is typically a white powdery or granular solid with a density of ~ 0.90 g/cc. This density is significantly lower than most forms of polyethylene, which means that less weight of polypropylene is required to make an article relative to polyethylene.

Unlike ethylene polymerization, regiochemistry and stereochemistry possibilities exist in propylene polymerizations. Usually, propylene adds in a "head-to-tail" manner with Ziegler-Natta catalysts, but the reverse mode of addition (a "regioerror") is also possible. As noted above, the methine carbon atom in the polymer structure (eq 1) is chiral which creates a variety of stereoisomeric possibilities. The configuration of the methyl group in the polymer chain is indicative of what is called the polymer's "tacticity." If the methyl groups are predominantly oriented in the same direction, the polymer is designated "isotactic," a nomenclature derived from the Greek word for "same" or "ordered" proposed by Natta (following a suggestion from his wife who was a linguist) [10]. Isotactic polypropylene is by far the most common form of industrial polypropylene and contains substantial crystalline content. If the methyl group uniformly alternates from side to side along the polymer chain, the stereoisomeric form is termed "syndiotactic," and, like isotactic, also contains substantial crystalline content. If the methyl group is randomly oriented, the polymer is termed "atactic" and is a rubbery, amorphous, tacky material, generally considered to be undesirable. However, at least one company purposely manufactures atactic polymer, which has uses as an adhesive, among other applications. The three most common stereoisomeric forms are schematically illustrated in Figure 1.2. A variety of polymorphic forms and other tacticities are possible, but will not be discussed here. However, more information on stereochemistry and regiochemistry of polypropylene will be provided in Chapter 2.

Melting characteristics of various forms of polypropylene have been studied and results are not as straightforward as one might expect [11, 12]. Nevertheless, the melting point (T_m) of isotactic polypropylene is

6 INTRODUCTION TO INDUSTRIAL POLYPROPYLENE

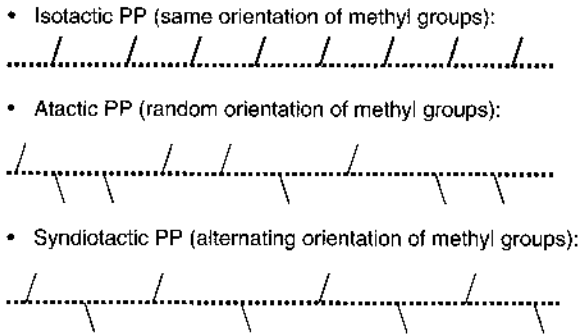


Figure 1.2 Schematic representation of stereoisomers of polypropylene. where dashed lines represent the “backbone” of the polymer and solid lines indicate configuration of methyl groups along the chain.

typically reported to be in the range 160–170°C. T_m may be affected by a range of factors, including tacticity, molecular weight, and thermal history. Copolymers have lower T_m and lower crystallinity.

Though polyethylene is the least costly of the major synthetic polymers, polypropylene has higher T_m and is tougher (higher modulus and tensile strength) and can be used in applications where these attributes make polypropylene the material of choice. Like polyethylene, stereoregular polypropylene is a thermoplastic with excellent chemical resistance and toughness and can be processed in a variety of ways. Injection molding, fiber extrusion and film extrusion are fabrication methods that account for nearly 90% of all polypropylene applications. More information on fabrication methods will be provided in Chapter 11.

Because of the tertiary carbon atom, polypropylene is especially prone to attack by oxygen in ambient air, commonly termed “autoxidation” (see section 11.2 and Figure 11.1). To minimize oxidative degradation, the raw polymer is usually melted immediately after manufacture and an antioxidant is introduced. (Additives are essential to improve stability and enhance properties of polypropylene. See section 11.2) The molten product is shaped into translucent pellets and supplied in this form to processors (Figure 1.3). Pelletization increases resin bulk density resulting in more efficient packing and lower shipping costs. It also reduces the possibility of dust explosions while handling.

As noted above, polypropylene is a thermoplastic material. That is, it can be melted and shaped into a form which can then be subsequently remelted and shaped (recycled) into other forms.



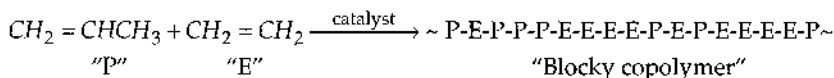
Figure 1.3 Raw polypropylene resin is melted and shaped into pellets of the type shown above. Pelletization increases bulk density, improves handling characteristics and reduces shipping costs. Pellet size is typically ~3 mm (or ~0.1 in). (Reproduced from *Introduction to Industrial Polyethylene*, with permission of Scrivener Publishing LLC).

Propylene may be copolymerized with a range of other olefins, such as ethylene and α -olefins (1-butene, 1-hexene, etc.). The other olefins are termed comonomers and are incorporated into the growing polymer chain. Some types of vinylic comonomers cannot be used. For example, Ziegler-Natta catalysts are usually poisoned by oxygen-containing polar comonomers such as vinyl acetate. Consequently, copolymers of propylene and VA are not available from Ziegler-Natta catalysts. However, certain single site catalysts are more tolerant of oxygen-containing compounds. Hence, copolymers of propylene with polar comonomers may be available from single site catalysts (see Chapter 6) in the not-too-distant future. Such copolymers may have unique properties and applications.

Ethylene is the most commonly used comonomer. Some products also employ higher alpha olefins (1-butene, 1-hexene, etc.). Often, the pattern of incorporation of comonomer along the polymer chain is not statistical because of differences in reactivity (see discussion of kinetics and reactivity ratios in Chapter 8). This results in nonuniformities in content and distribution of comonomers along the polymer chain. This is called the composition distribution (CD) and may be determined by ^{13}C NMR analysis in combination with chromatographic methods discussed in Chapter 2.

8 INTRODUCTION TO INDUSTRIAL POLYPROPYLENE

Of course, regioerrors are not possible when ethylene is incorporated as comonomer, since carbons are equivalent. However, the polymer chain may contain "blocks" of ethylene units resulting from multiple insertions. This heterogeneity is termed "blockiness" and is represented schematically below.



In addition to blockiness, alpha-olefin comonomers (1-butene, 1-hexene, etc.) may be incorporated in ways that result in regioerrors.

When propylene is copolymerized with large amounts (>25%) of ethylene, an elastomeric copolymer is produced, commonly known as ethylene-propylene rubber (EPR) or ethylene-propylene monomer (EPM) rubber. When a diene, such as dicyclopentadiene, is also included, a terpolymer known as ethylene-propylene-diene monomer (EPDM) rubber is obtained. EPR and EPDM may be produced with single site and Ziegler-Natta catalysts and are important in the automotive and construction industries. However, EPR and EPDM are produced in much smaller quantities (~1 million mt/y) relative to polypropylene. Moreover, EPR and EPDM are amorphous, while the most important type of industrial polypropylene ("isotactic") has substantial crystalline content. Accordingly, these elastomers are considered outside the scope of this text and will not be discussed further. However, random copolymers and impact copolymers are important products involving propylene and ethylene (at levels up to about 25%) and will be addressed in this text.

End groups of propylene polymers are most often saturated (simple alkyl groups). This is largely a consequence of using hydrogen as chain transfer agent. However, there are low levels of unsaturated sites owing to termination reactions by chain transfer *via* β -hydride elimination and hydride transfer to monomer. Termination reactions are addressed in the context of the mechanism of polymerization in Chapter 3.

Of course, there is abundant short chain branching (SCB) in polypropylene owing to the methyl group of propylene and other alpha olefins that are occasionally used. By convention, SCB implies 6 or fewer carbons. Long chain branching (LCB) in polypropylene is very low and is difficult to detect *via* the usual analytical methods [13].

Several grades of polypropylene are used in food packaging, *e.g.*, blown film for candy and snack foods. In Europe, Canada, Japan, the USA and other developed countries, the resin must satisfy governmental regulations for food contact. Catalyst residues are quite low in modern polypropylene and are considered to be part of the basic resin. In the USA, the resin (including additives; see Chapter 11) must be compliant with FDA requirements for food contact, such as hexane extractables. The procedure for registration of polymers with governmental agencies can be complicated and protracted. Normally, the registration specifies the permitted uses.

Polypropylene is available in a dizzying array of compositions, with different microstructures, various comonomers, a range of molecular weights, *etc.*, predicated by selection of catalyst, polymerization conditions and other process options. Since 1951, when a small quantity of a crystalline polymer was obtained unexpectedly from a laboratory experiment in Bartlesville Oklahoma, stereoregular polypropylene has grown enormously and is used today in megaton quantities in innumerable consumer applications. Though all forms of polyethylene (HDPE, LDPE, EVA, LLDPE, *etc.*) if taken together, remain the largest volume plastic, a recent analysis suggests that polypropylene is the *single* largest volume plastic produced globally, exceeding even that of HDPE which is the largest type of polyethylene manufactured. Global polypropylene production in 2010 was estimated to be about 48 million metric tons (~106 billion pounds) [14].

1.3 Types and Nomenclature of Polypropylene

The most important types of commercially available polypropylene are:

- homopolymer (HP)
- random copolymer (RACO, aka RCP)
- impact copolymer (also called heterophasic copolymer or HECO, aka ICP)

Key characteristics of each major type of polypropylene are summarized in Table 1.1. Figure 1.4 shows the approximate percentages of each type sold into the merchant market in 2008. The polymer produced in eq 1.1 is known as polypropylene or poly (propene).

Table 1.1 Characteristics of types of polypropylene.

Type of PP*	Abbreviation	Typical Olefin Comonomer	Range of Comonomer Content (wt %)	Impact Resistance	Film Clarity	Tensile Strength
Homopolymer	HP	none	0	poor	poor	good
Random Copolymer	RACO	ethylene	1-7	medium	good	medium
Heterophasic Copolymer (aka impact copolymer)	HECO (ICP)	ethylene	5-25	good	na**	poor

* Densities of HP, RACO and HECO are all in the range 0.89-0.91 g/mL

** Not applicable

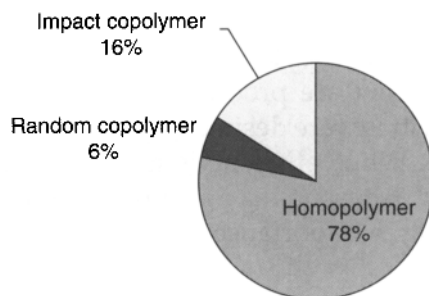


Figure 1.4 Types of industrial polypropylene in market in 2008. The total market in 2008 was estimated to be about 46 million metric tons (~101 billion pounds). Source: C. Lee and B. Singh, Chemical Marketing Research, Webster, TX, June, 2009.

Either is an acceptable name for homopolymer, according to IUPAC. However, polypropylene is by far the more commonly used name in industry and will be used exclusively in this text.

IUPAC nomenclature for copolymers is also not commonly used in industry. Since ethylene is the comonomer most often employed for RACO and HECO, the IUPAC name for such copolymers would be poly (propylene-*co*-ethylene).

Abbreviations for polypropylene are sometimes used to indicate the catalyst employed in its production or its stereochemistry. For example, polypropylene produced with metallocene catalysts (see Chapter 6) are often designated mPP. Isotactic and syndiotactic polypropylene are sometimes abbreviated iPP and sPP, respectively.

In addition to the nomenclature discussed above, manufacturers use their own registered trademarks. There are far too many trade names to include a comprehensive listing here, but examples are given below (along with the company that owns the trademark).

- Pro-fax (LyondellBasell)
- Vistamaxx (ExxonMobil)
- Achieve (ExxonMobil)
- VERSIFY (Dow)
- Fortilene (Solvay)
- Innovene (INEOS)
- INSPIRE (Braskem)
- Marlex (Chevron Phillips)
- Clyrell (LyondellBasell)
- Borstar (Borealis)
- TAFMER (Mitsui)

12 INTRODUCTION TO INDUSTRIAL POLYPROPYLENE

As is evident from Figure 1.4, more than three-quarters of the global industrial polypropylene market is homopolymer. Lesser amounts of copolymer are produced for specialized applications where specific attributes are desired, such as film clarity or superior impact resistance. While ethylene is most often used as comonomer, 1-butene and 1-hexene may also be used. Moreover, terpolymers are increasing in importance.

1.4 Molecular Weight of Polypropylene

Polypropylene manufacturers routinely supply data that correlate with molecular weight and molecular weight distribution. A measurement called the melt flow rate (MFR) is determined by the weight of polypropylene extruded over 10 minutes at 230°C through a standard die using a piston load of 2.16 kg. Reported in g/10 min or dg/min, melt flow rate is measured using an instrument called an *extrusion plastometer* (see Figure 1.5.) according to ASTM D 1238–04c Condition 230/2.16, where the latter numbers refer to the temperature and the load in kg on the piston of the plastometer, respectively. Melt flow rate is inversely proportional to molecular weight, *i.e.*, molecular weight decreases as MFR increases.

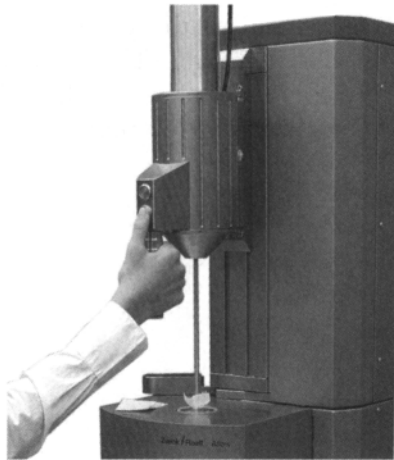


Figure 1.5 Melt flow rate of polypropylene may be measured on an instrument called an extrusion plastometer. (Photo courtesy of Zwick/Roell.)

The term melt index (MI) is sometimes applied (erroneously) to the low load MFR for polypropylene. ASTM suggests that MI (determined at 190°C) be reserved for polyethylene and MFR be used for all other plastics, regardless of conditions used (see note 27 on p 10 of ASTM D 1238-04c).

Another melt flow rate value for polypropylene may also be measured on the plastometer at 230°C, but under a load of 21.6 kg (ASTM D 1238-04c Condition 230/21.6). This MFR is also reported in g/10 min or dg/min. Dividing the MFR measured at high load by the MFR at low load affords what is called the flow rate ratio (FRR) as in eq 1.2. FRR is a dimensionless number which gives an

$$\text{FRR} = (\text{MFR @ 21.6 kg}) \div (\text{MFR @ 2.16 kg}) \quad (1.2)$$

indication of breadth of the molecular weight distribution. As FRR increases, MWD broadens.

MFR and FRR measurements are inexpensive, relatively easy to conduct and are indicative of molecular weight and molecular weight distribution. Actual molecular weights may be determined using a variety of analytical methods, including gel permeation chromatography (GPC), viscometry, light scattering and colligative property measurements. (GPC is also called size exclusion chromatography or SEC.) However, these methods require more sophisticated instruments that are usually operated by highly trained technical personnel. Procedures are more costly and difficult to perform and do not lend themselves to routine quality control. Nevertheless, expressions having to do with molecular weight and molecular weight distribution of polypropylene obtained using these instrumental methods often appear in discussions of PP properties in patent and journal literature. The most important values are called the number average molecular weight (\bar{M}_n) and the weight average molecular weight (\bar{M}_w). The ratio \bar{M}_w/\bar{M}_n is called the polydispersity index (PDI, also known as heterogeneity index and dispersity index) and is an indication of the broadness of molecular weight distribution. As polydispersity index increases, MWD broadens. Polydispersities typically range from 4-8 for polymer produced with Ziegler-Natta catalysts. However, polypropylene made with single site catalysts show polydispersities of 2-3 indicating a much narrower MWD.

The number average molecular weight (\overline{M}_n) is calculated from the expression:

$$\overline{M}_n = \sum M_x N_x / \sum N_x \quad (1.3)$$

where M_x is the molecular weight of the x^{th} component and N_x is the number of moles of the x^{th} component. Weight average molecular weight (\overline{M}_w) is calculated using the second order equation:

$$\overline{M}_w = \sum M_x^2 N_x / \sum M_x N_x \quad (1.4)$$

The third order equation provides the "z-average molecular weight" and is calculated from the expression:

$$\overline{M}_z = \sum M_x^3 N_x / \sum M_x^2 N_x \quad (1.5)$$

Higher order molecular weight averages may also be calculated, but are less important than \overline{M}_w , \overline{M}_n and \overline{M}_z . For polydisperse polymers, such as polypropylene, the following relationship holds:

$$\overline{M}_z > \overline{M}_w > \overline{M}_n$$

Direct comparisons between melt flow rate and molecular weight of polypropylene should be made with caution. Such comparisons are appropriate only when the polymers have similar histories (made using the same catalyst, by the same process, etc.). An example of the relationship between melt flow rate and weight average molecular weight (determined from intrinsic viscosity) for polypropylene with similar histories is shown in Figure 1.6. However, polypropylene used in the latter study was produced using early generation ZN catalysts. An equation relating melt flow rate and molecular weight has also been published for "modern" polypropylene [15]:

$$\log \text{MW} = (-0.2773 \times \log \text{MFR}) + 5.7243$$

A graphical representation of the relationship between MFR and intrinsic viscosity for polypropylene prepared with modern ZN catalysts was shown by Del Luca, *et al.* [16]. Molecular weight measurement is discussed further in Chapter 2.

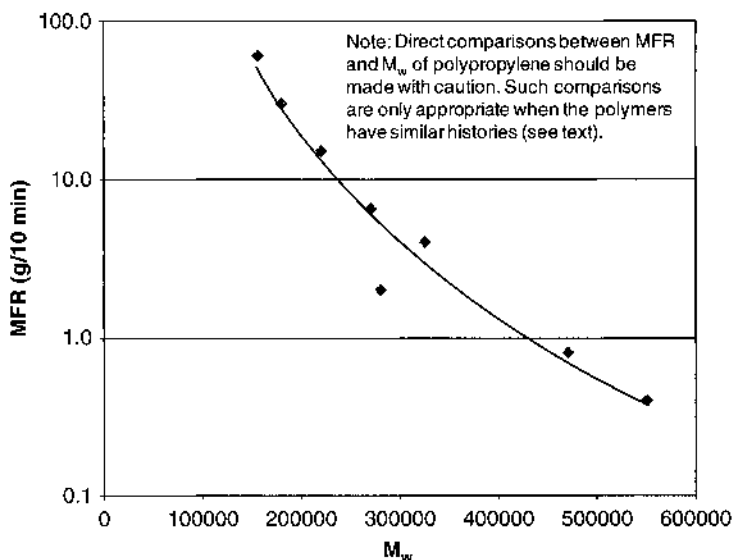


Figure 1.6 M_w vs. MFR for PP homopolymer. (from E. Vandenberg and B.C. Repka, *High Polymers*, John Wiley, 29, 365, 1977)

1.5 Transition Metal Catalysts for Propylene Polymerization

As previously mentioned, propylene may be polymerized by use of transition metal catalysts. To put these in perspective, one must recognize that transition metal catalysts have been used to produce virtually 100% of the cumulative trillion+ pounds of the global industrial output of polypropylene since commercial operations began in 1957. Transition metal catalysts are at the very heart of commercial processes used to manufacture polypropylene. Indeed, industrial polypropylene would be essentially unknown without transition metal catalysts.

In this section, we will introduce key characteristics of transition metal catalysts. From the standpoint of industrial polypropylene, Ziegler-Natta catalysts are by far the most important. Additional details on Ziegler-Natta catalysts will be provided in Chapters 3 and 4. As noted in section 1.2, the two most important catalysts are Ziegler-Natta and single site, both to be discussed in more detail in subsequent chapters. "Metallocene" catalysts (Chapter 6) may

be considered to be a subset of what are more broadly designated as "single site catalysts." However, not all metallocenes are effective as catalysts for propylene polymerization and not all single site catalysts are metallocenes.

Polypropylene catalysts are most often produced using compounds from Groups 4–6 of the Periodic Table. Cocatalysts are required with all industrial versions of polypropylene catalysts. (Single site catalysts that do not require cocatalysts have been discovered, but are not yet used in industrial processes for polypropylene). In the vast majority of catalyst systems, alkylaluminum compounds (see Chapter 5) are used as cocatalysts. Modern Ziegler-Natta catalysts for polypropylene, are usually derived from inorganic titanium compounds and are most often supported on magnesium chloride. Industrial single-site catalysts (Chapter 6) commonly involve metallocene compounds of Zr, Hf or Ti. Non-metallocene single site catalysts based on late transition metals, especially Pd, Fe and Ni, began to emerge in the mid-1990s, though these are not industrially significant at this writing.

For industrial viability, transition metal catalysts for polypropylene must fulfill several key criteria:

- Activity must be high enough such that catalyst residues are sufficiently low in the final polymer to obviate post-reactor treatment to remove catalyst residues. As a rule of thumb, this requires that catalyst activity exceed about 150,000 lb of polypropylene per lb of transition metal.
- The catalyst must polymerize propylene with proper stereochemical control. In most industrial polypropylene processes, the desired stereoisomer is the isotactic version. Obtaining product with high isotactic content (usually >94%) makes it possible to forgo costly steps to remove atactic content.
- The catalyst must polymerize propylene with minimal "regioerrors." That is, polymerization must be selectively "head-to-tail" (see discussion in section 2.2.1).
- The catalyst must be capable of providing a range of polymer molecular weights. For Ziegler-Natta and single site catalysts, molecular weight is controlled primarily by use of hydrogen as chain transfer agent. Catalyst reactivity with hydrogen to control polymer molecular weight is called its "hydrogen response."

- Control of polydispersity is achieved primarily with the catalyst. Though each type of catalyst provides polypropylene with a characteristic range of molecular weight distributions, measures can be taken to expand marginally the range of achievable polydispersities. PDI are typically 4–8 for Ziegler-Natta catalysts and 2–3 for single site catalysts.
- If a RACO or HECO is the target resin, amounts and regiochemistry of comonomer incorporation must be acceptable. Quantities of comonomer, as well as the uniformity of incorporation (or lack thereof), are measures of whether satisfactory copolymerization has occurred. For example, a “blocky” copolymer is sometimes desired. (“Blockiness” of a copolymer can be determined by analysis of its composition distribution.)

Additional details will be provided in subsequent chapters on the composition and functioning of transition metal catalysts.

As noted above, transition metal catalysts are essential for the manufacture of polypropylene. It is not hyperbole to state that production of stereoregular polypropylene would not be possible without these catalysts. It is difficult to imagine a world without the huge number of products made from these versatile polymers in our homes, vehicles and workplaces. Ziegler-Natta will continue to be the dominant catalysts for the various forms of polypropylene well into the 21st century. However, as single site catalyst technologies mature, they will increase in importance and complement Ziegler-Natta catalysts in manufacture of polypropylene.

1.6 Questions

1. Who was the first to prepare crystalline polypropylene? When?
2. What percentage of industrial polypropylene is manufactured with Ziegler-Natta catalysts?
3. What are the three principal types of industrial polypropylene and what is the approximate percentage of each?
4. Why are copolymers of propylene with vinyl acetate not commercially available?

5. What is melt flow rate? How is it measured? What is its significance?
6. What is FRR? What is its significance?
7. What is the polydispersity index? What is its significance?
8. Provide key criteria for performance of industrial polypropylene catalysts.

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