

# Ziegler–Natta Polymerization and the Remaining Challenges

*Samir H Chikkali*

Polymers have become indispensable in the 21st century, and today we cannot imagine life without them. However, till around the beginning of the last century, the science of polymers was considered a very primitive discipline, and majority of the scientific community did not believe that polymers even existed. Hermann Staudinger, among others, fought a long battle to convince the scientific community that polymers are real and that they are long chain molecular entities. Building on this rational bedrock of polymer science, Prof. Karl Ziegler laid the foundation of ethylene polymerization. As outlined by Dr. Sivaram in his articles on Ziegler and Natta, careful observations and systematic analyses of serendipitous results enabled Ziegler to develop the enormously significant ‘Mülheim atmospheric polyethylene process’. A decade later, Cossee and Arlman revealed the mechanism of this polymerization reaction, which is called ‘insertion polymerization’. Insertion polymerization is popularly known as the ‘Ziegler–Natta polymerization’, in recognition of its founding fathers. Today, the world produces about 180 million tons of polyolefins annually, and polyethylene or polythene has become a household name.

In this article, I shall present an overview of Ziegler–Natta polymerization. I will highlight the mechanism of this reaction, and outline the progress made in the last seven decades using some real-world examples. The last part of this article will take a stock of the unresolved challenges posed by Ziegler–Natta polymerization, briefly discuss current solutions, and reiterate the enormous potential of this seventy-year-old reaction to meet contemporary challenges.



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## Keywords

Insertion polymerization, copolymers, polyethylene, Ziegler–Natta catalyst, Cossee–Arlman mechanism, functional polyethylene, difunctional olefins.



The practical importance of polymers led to widespread interest in academic and industrial research laboratories, and the decades between 1930 and 1950 witnessed the emergence and commercialization of a variety of polymers.

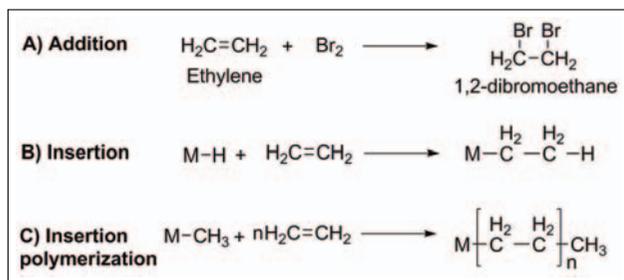
## 1. Introduction

Human civilization, from time immemorial, has relied on polymers. Natural polymers like cotton, silk, wool, and gum were known to humankind since a very long period and have contributed significantly to shape our history. However, until the turn of the century, the science of polymers remained a primitive discipline, without a fundamental molecular understanding. In 1920, Hermann Staudinger proposed that polymers consist of long chains. While this appears obvious to us now, it took him almost 30 years to convince the scientific community that polymers are indeed long chain macromolecules. Another Herman, Herman Mark, contributed to the fundamentals of polymers. The foundations of rational ‘polymer science’ were laid primarily by these two Hermans. The practical importance of polymers led to widespread interest in academic and industrial research laboratories, and the decades between 1930 and 1950 witnessed the emergence and commercialization of a variety of polymers – from polyvinyl chloride (PVC) to polyethylene (PE). The metal-catalyzed polymerization of ethylene to polyethylene by Prof. Karl Ziegler is one of the most disruptive discoveries of the 20th century. Today, we annually produce about 180 million tons of polyolefins using the very same reaction that Prof. Ziegler discovered in 1954. In this article, I will briefly explain this reaction and how it marked the beginning of a material that we come across every day in our daily lives. I will quickly review the progress made since this discovery and what has been achieved in the last seven decades, the current state-of-the-art, and the remaining challenges.

## 2. What is Insertion Polymerization?

You’ve probably learned about various organic reactions such as addition, substitution, and elimination in high school and college. A classical example of an addition reaction is the one attributed to Markovnikov. In a Markovnikov type addition reaction, bromine is added across a carbon-carbon double bond of an





**Figure 1.** (A) Markovnikov type addition reaction, (B) Insertion of ethylene in a metal-hydride, and (C) Insertion polymerization of ethylene.

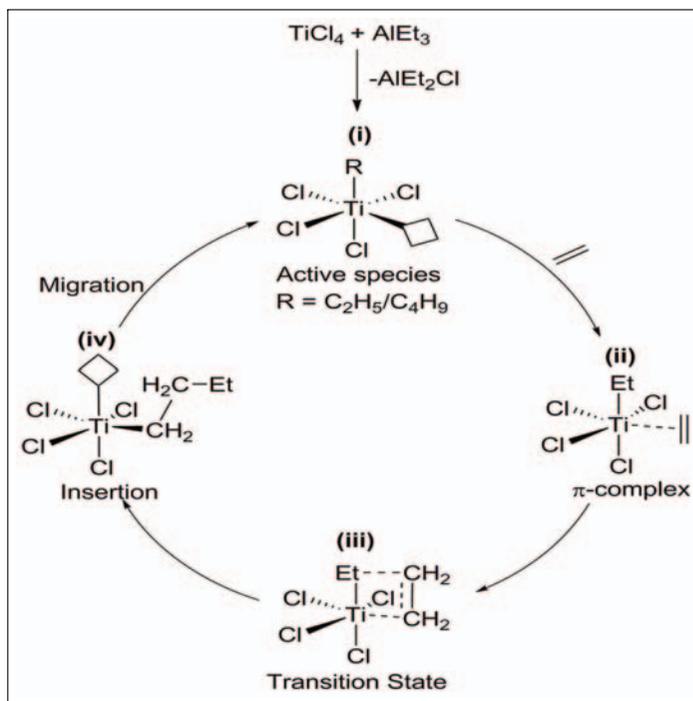
In an insertion reaction, interposition and insertion of a new element or entity in-between an existing metal-C or metal-H bond takes place.

ethylene molecule to obtain 1, 2-dibromoethane (*Figure 1(A)*). A very special class of such addition reactions is an insertion reaction. In an insertion reaction, interposition and insertion of a new element or entity in-between an existing metal-C or metal-H bond takes place. As depicted in *Figure 1(B)*, an ethylene molecule is inserted into the M-H bond.

Along the same lines, in an insertion polymerization, insertion of ethylene (a neutral donor molecule) in a metal-C or metal-H bond takes place, and repetition of this step leads to the production of polyethylene. Thus, in an insertion polymerization reaction, each ethylene molecule delivers two carbon atoms to the M-C/H bond and the process of insertion is repeated several times to obtain a high molecular weight macromolecule. This is the very reaction that Ziegler perfected to obtain polyethylene. As highlighted by Dr. Sivaram in the first part of this issue, the discovery of insertion polymerization reaction by Ziegler was not so much of a serendipitous observation as it was a systematic exploration. It was guided by experimental observations and was an outcome of rational and systematic experimentation. Although the insertion reaction might appear very simple in *Figure 1(C)*, the experimental reality is different. Several proposals were made to explain this reaction among which, the Cossee–Arlman mechanism is generally accepted today. But, note that it took Cossee and Arlman more than a decade to propose a realistic and well-accepted mechanism for the insertion polymerization of ethylene. Insertion polymerization is popularly known as ‘Ziegler–Natta’ (Z–N) or ‘coordination’ polymerization.



**Figure 2.** Cossee–Arlman mechanism for insertion polymerization of ethylene.



Insertion polymerization was found to take place in the presence of two compounds in general: group IV metal halides and alkyl aluminium, particularly, titanium tetrachloride ( $\text{TiCl}_4$ ) and triethylaluminium ( $\text{AlEt}_3$ ). After the groundbreaking discovery of Ziegler and Natta, various mechanisms were proposed to explain the mode of action of the Ziegler catalyst in olefin polymerization. The founding fathers, Prof. Ziegler and Prof. Natta, initially proposed a bimetallic mechanism. However, detailed mechanistic investigations by Cossee and Arlman established that the insertion polymerization follows a monometallic mechanism and that the polymerization takes place at the transition metal–carbon bond [1].

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The metal-catalyzed insertion polymerization deviates from the standard radical or condensation polymerization. The first step in insertion polymerization is the formation of an active metal complex, called the ‘active species’. Cossee and Arlman proposed that the first step in an insertion polymerization is *trans-*

metallation between  $\text{TiCl}_4$  and  $\text{AlEt}_3$  to generate a titanium-alkyl species (*Figure 2(i)*). This is followed by coordination of ethylene to form a  $\pi$ -complex. The  $\pi$ -complex (*Figure 2(ii)*) is stabilized through the donation of  $\pi$ -electrons of ethylene to the vacant titanium  $\text{dx}^2\text{-y}^2$  orbital and back-donation from the filled titanium d ( $\text{d}_{yz}$ ) orbital to the empty  $\pi^*$  orbital of ethylene. Next, the titanium-alkyl bond is polarized, and the methylene carbon attacks one of the ethylene carbons to yield a four-membered transition state as in (*Figure 2(iii)*). In the last event, ethylene inserts into the metal-methylene-carbon bond and one ethylene molecule is added to the starting species (i). The insertion of ethylene leads to the creation of a vacant site, but at a different place than the original vacant site. This closes the catalytic cycle, and two carbon atoms are delivered to the initial species. Repeated insertion of ethylene as depicted in *Figure 2* results in the formation of a long polyethylene chain. This scenario for ethylene polymerization is also valid for the polymerization of other olefins such as propene, butene, hexene, octene, decene and so on. But, can you extend the same reaction to functional alkenes such as acrylic acid or vinyl chloride? Would a Ziegler catalyst allow insertion polymerization of vinyl chloride or acrylic acid? I leave this discussion for you to think over and will return to it later in this article.

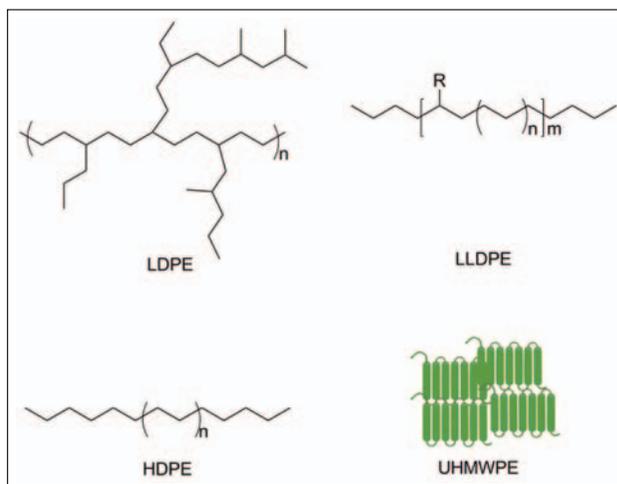
Would a Ziegler catalyst allow insertion polymerization of vinyl chloride or acrylic acid?

### 3. Real World Polymers by Insertion Polymerization

Having learned about the insertion reaction and the concept of insertion polymerization, let us examine how this chemistry impacts our daily life. The fundamental scientific discovery made by Ziegler–Natta had to be translated into an industrial process to meet societal needs. A low-pressure industrial process was developed, based on insertion polymerization and was named the ‘Mülheim atmospheric polyethylene process’. Tremendous progress in this chemistry has been made over the decades, and today, we produce staggering quantities of polyolefins using this low-pressure process. The most commonly encountered polymer prepared by this process is polyethylene that we encounter in the



**Figure 3.** Structural differences between LDPE, LLDPE, HDPE, and cartoon representation of UHMWPE.



familiar ‘carry bags’. Of course, the humble carry bag is only one of the products made using polyethylene, and there are many more applications of this class of polymers.

Polyethylene can be classified into four main categories: 1) Low Density Polyethylene (LDPE), 2) Linear Low Density Polyethylene (LLDPE), 3) High Density Polyethylene (HDPE), and 4) Ultra High Molecular Weight Polyethylene (UHMWPE). Representative chemical structures of these polymers are depicted in *Figure 3*.

Polypropylene is also prepared using Ziegler–Natta catalyst and currently brings enormous benefits to the society.

Polypropylene (PP) is also prepared using Ziegler–Natta catalyst and currently brings enormous benefits to the society (*Table 1*).

Among the various polyethylenes, low density polyethylene (LDPE) with density  $\leq 0.930 \text{ g/cm}^3$  is characterized by significant levels of long chain branching. Some of the common applications of LDPE are summarized in *Table 1*. Linear low density polyethylene (LLDPE) with a density of  $0.915\text{--}0.925 \text{ g/cm}^3$  can be produced using Ziegler–Natta system by incorporating small amounts of  $\alpha$ -olefins into the PE backbone. Due to its higher tensile strength and tear resistance, LLDPE is routinely used to manufacture films (*Table 1*). High density polyethylene (HDPE, density =  $0.940\text{--}0.965 \text{ g/cm}^3$ ) is a linear polyethylene without branching and is more crystalline than LDPE and LLDPE. Due to its high density



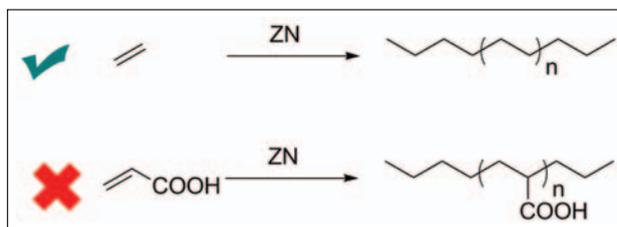
Polymer Type	Representative Applications	Manufacturers
LDPE	Bottle caps, closures, food packaging containers, houseware articles, toys, trays.	Borealis, Reliance Industries Limited, ExxonMobil.
LLDPE	Food packaging films agricultural packaging, cast films, blown films, and various film and packaging applications.	Total, Borealis, Reliance Industries Limited, ExxonMobil, Gas Authority of India Limited, Mitsui Chemicals.
HDPE	LAN cables, telecom wires, thermoplastic jacketing, industrial pails, vegetable crates, boxes, heavy duty crates.	Ineos, Total, Borealis, Reliance Industries Limited, ExxonMobil, Gas Authority of India Limited, Mitsui Chemicals.
UHMWPE	Cut resistant gloves, medical implants such as hip and knee joints, body armors, military helmets, climbing equipment, fishing lines, bow strings, spear lines, suspension lines on sports parachutes, paragliders.	DSM, Mitsui Chemicals, LyondellBasell, Honeywell.
PP	Melt blown fibers, medical gowns, covers, and medical packaging, labwares, diapers, wet wipes, disposals, and housewares.	Indian Oil Corporation Limited, Reliance Industries Limited, Mitsui Chemicals.

and increased crystallinity, HDPE is used to manufacture heavy-duty items as indicated in *Table 1*. Polyethylenes with molecular weights ( $M_w$ ) over 1 million are called ultra high molecular weight polyethylenes (UHMWPE). Due to their very high molecular weight, these polymers are strong and sturdy materials that find use in demanding applications as listed in *Table 1*.

**Table 1.** Real world polymers created by insertion/Ziegler–Natta polymerization and their commercial applications.



**Figure 4.** Z–N/Insertion polymerization of non-functional (top) versus functional (bottom) olefins.



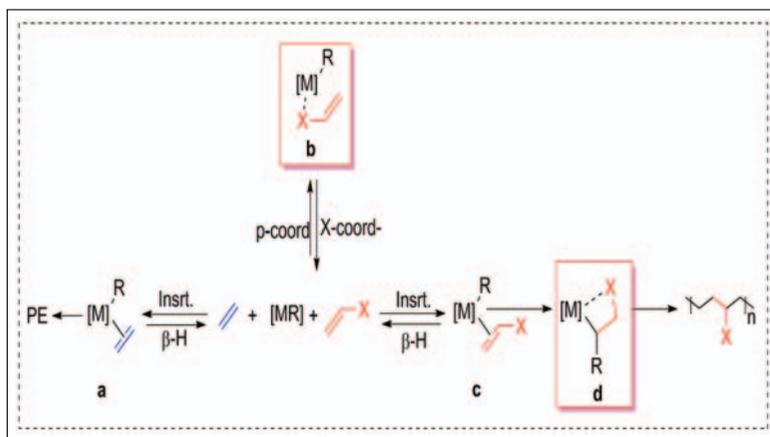
#### 4. Ziegler–Natta/Insertion Polymerization and the Remaining Challenges

The high oxophilicity of early transition-metal polymerization catalysts employed in traditional Z–N systems leads to catalyst poisoning by strong  $\sigma$ -coordination of the Lewis basic moiety of functional vinyl monomers.

As we discussed in the earlier sections, the seminal work of Ziegler and Natta laid the foundation of insertion polymerization, and the product of this reaction has reached every nook and corner of this planet. Having said that, let me return to the questions I posed earlier, regarding the extension of this reaction to olefins carrying functional groups. Z–N polymerization of non-functional olefins such as ethene, propene, butene, hexene, and octene is well established. However, if you wish to make what appears like a small change and attempt Z–N polymerization of functional olefins such as acrylic acid, then this reaction fails and polymerization does not take place (*Figure 4*). If we can pin down the reasons behind this failure, we might be able to design strategies that will enable Z–N-like polymerization of functional olefins. Polyolefins incorporating functional olefins have a wide variety of applications. This has prompted a major review of Z–N chemistry to rationally design strategies for functional olefin polymerization. The high oxophilicity of early transition-metal polymerization catalysts employed in traditional Z–N systems leads to catalyst poisoning by strong  $\sigma$ -coordination of the Lewis basic moiety of functional vinyl monomers. Therefore, a strategy that is currently being explored for insertion copolymerization<sup>1</sup> of ethylene with polar vinyl monomers is to switch to late-transition-metal catalysts (LTM) that are generally, more tolerant towards functional groups.

Even with LTM, there are at least three (if not more) fundamental challenges that hamper insertion polymerization of functional

<sup>1</sup>When two or more monomers react with each other to form a polymer containing repeating units from both the monomers, the resultant polymer is called a ‘copolymer,’ and the process of formation of a copolymer is called ‘copolymerization.’ For example, ethylene and propylene can react to yield copoly(ethylene-propylene) or ethylene-propylene copolymer.



**Figure 5.** The major challenges in functional olefin copolymerization.

olefins using Z–N systems (Figure 5). The success of insertion polymerization of functional olefins will heavily rely on how we can address these fundamental challenges. First and foremost hurdle is the coordination of the functional group to the metal to form a  $\sigma$ -complex, leading to catalyst deactivation. Secondly, functional olefins are relatively electron deficient, and there is less electron density around the double bond. In a coordination competition between the two olefins to the metal, the non-functional olefin (such as ethylene) wins over the electron deficient functional olefin (such as acrylic acid) due to its poor  $\pi$ -donating ability. As a result, only PE is obtained, without any incorporation of the functional olefin (Figure 5(a)). Even if we manage to overcome these two problems, we are faced with the formation of a stable chelate (Figure 5(d)), after the insertion of the functional olefin. Formation of such a stable chelate halts the growing polyolefin chain. A paradigm shift in the insertion copolymerization of functional olefins can be achieved only if these fundamental challenges can be addressed efficiently. However, even the most successful catalytic systems that define the current state-of-the-art only partly satisfy these criteria. Thus, even these enable incorporation of functional olefins only to a limited extent.



#### 4.1 Ziegler–Natta/Insertion Copolymerization of Fundamental Functional Olefins

There are currently five state-of-the-art catalytic systems that have been successful in yielding functionalized polyethylenes.

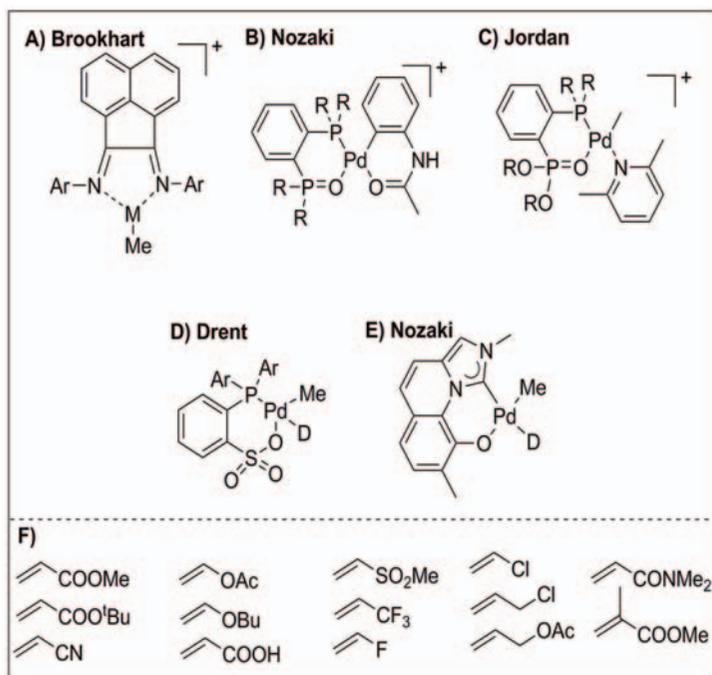
Insertion copolymerization of functional vinyl monomers has been on the radar of the research community for quite a while. Initial reports claimed insertion copolymerization of polar vinyl monomers using classical Z–N systems. However, these were later shown to proceed *via* a more common radical pathway, rather than through a true insertion mechanism. As depicted in *Figure 6*, there are currently five state-of-the-art catalytic systems that have been successful in partially addressing the aforementioned challenges to yield functionalized polyethylenes.

In a pioneering work in 1995, Brookhart and co-workers reported that cationic nickel and palladium diimine complexes (*Figure 6(A)*, Brookhart systems) successfully copolymerize ethylene with methyl acrylate (MA), a functional olefin. Powered by a clever choice of late-transition metal and aided by the diimine ligand, insertion copolymerization of MA with ethylene was successfully achieved for the first time [2]. The polymer obtained was highly branched with acrylate functionalities located at branch extremities due to extensive ‘chain-walking’<sup>2</sup>. Capitalizing on this initial work, insertion copolymerization of various polar vinyl monomers using cationic  $\alpha$ -diimine palladium complexes was explored. A series of ligands with tailored electronic and steric constraints were screened for their efficacy in copolymerization, although with limited success since only low polymer molecular weights could be obtained (*Figure 7*) [3]. In a significant advancement, Chen and co-workers recently modulated the Brookhart catalyst to obtain functionalized copolymers with high molecular weights. Their trick? They found that installation of highly bulky Ar-groups (*Figure 7*, extreme right, Ar = Naphthalene) yielded high molecular weight copolymers.

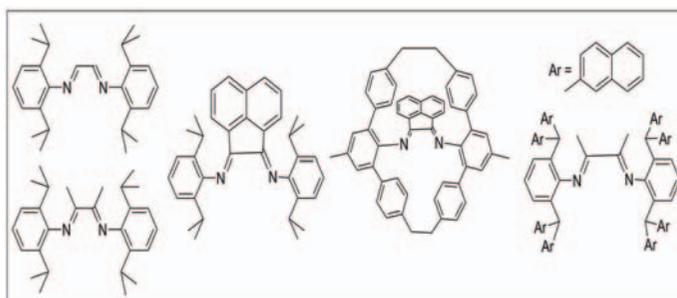
Another cationic LTM system that has been found to copolymerize ethylene with functional olefins is the bis-phosphine monoxide palladium complex B. Nozaki and co-workers recently designed a neutral ligand called bis-phosphine monoxide (BPMO).

<sup>2</sup>Migration of the insertion site along the chain.





**Figure 6.** State-of-the-art functional olefin polymerization catalysts (top) and the functional olefins utilized (bottom).



**Figure 7.** Modification of Brookhart's  $\alpha$ -diimine ligand system.

The reactivity of palladium complexes derived from BPMP chelating ligand was investigated in the insertion copolymerization of polar vinyl monomers with ethylene. The cationic palladium complexes ligated by BPMP were found to copolymerize ethylene with a number of polar vinyl monomers, including historically challenging functional olefins such as vinyl acetate, acrylonitrile, and vinyl ethers [4].

Although cationic group 10 complexes ligated by a BPMP ligand

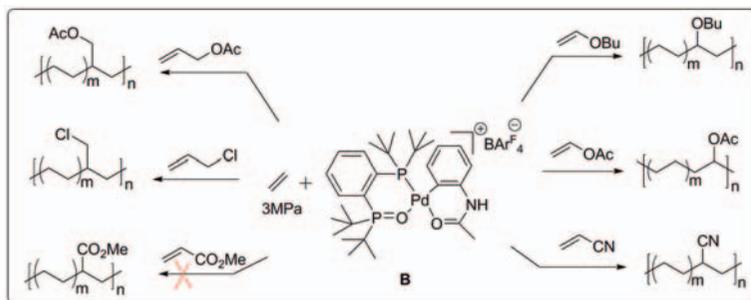


have been previously shown to oligomerize ethylene, installing aliphatic substituent on the phosphine/phosphine-oxide phosphorus led to the production of high molecular weight copolymers. Consistent with the earlier literature, the lowest molecular weight copolymers were produced when the substituents on phosphine phosphorous were phenyl groups. Such a drastic substituent effect has been rationalized using the single crystal X-ray structure of the complex and postulating the electronic effects due to this structure. Thus, the electronic properties of BPMP ligands that contain alkyl phosphine oxide substituents appear to be distinctly different than other (P, O)-type ligands (such as *Figure 6* (C) and (D)). Another major difference between the Brookhart system and the BPMP system was the placeholder ligand D (*Figure 6*(B)). Single component group 10 metal pre-catalysts typically possess a stabilizing ligand (*i.e.*, ethers, amines, pyridine, and phosphine) that affects the initiation and/or propagation steps by competing with the monomer for coordination to the metal center. One strategy to mitigate this kinetic impediment is the use of weakly coordinating ligands, such as dimethyl sulfoxide (DMSO) or acetonitrile that can be readily displaced by ethylene. Alternatively, a palladacycle in which a native ligand is directly appended on the carbon ligand can be used. However, group 10 metal catalysts containing this structural motif are very rare. The Nozaki system (*Figure 6*(B)) utilizes this concept by featuring an amide motif, which acts as a placeholder ligand. An additional advantage of such a motif is that the motif is incorporated into the polymer chain upon insertion of ethylene into the palladium-phenyl bond during initiation and is subsequently removed from the proximity of the metal during propagation.

Incorporation of the functional monomer at both the chain ends as well as in the main chain was observed for polar vinyl monomers when (B) (*Figure 8*) was used as the catalyst. Enchainment of the polar monomer into these polymers ranged from 0.7–4.1 mol%, which compares well with the Brookhart system. The reactivity of cationic BPMP-palladium complexes is in contrast with the trends observed for other cationic palladium catalysts. For

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**Figure 8.** Insertion copolymerization of ethylene with polar vinyl monomers using cationic bisphosphine monoxide palladium catalysts (B).

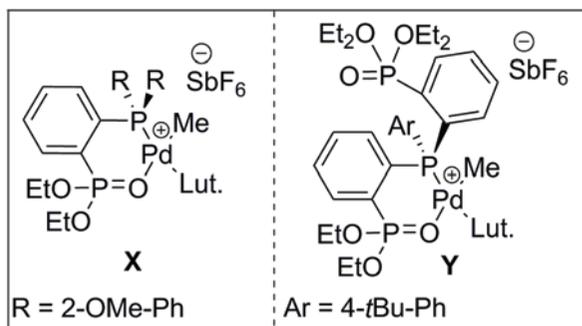
The cationic Brookhart catalysts afford varying degrees of branching depending on the ligand structure, ethylene pressure, and reaction temperature.

instance, the cationic Brookhart catalysts afford varying degrees of branching depending on the ligand structure, ethylene pressure, and reaction temperature, but the polyethylene and random poly(ethylene-co-functional olefin) copolymers produced by cationic BPMO palladium catalysts are always linear. The BPMO-palladium complexes were found to tolerate polar vinyl monomers that readily deactivate the catalyst by  $\beta$ -elimination of the functional group (*e.g.*, vinyl acetate and vinyl ethers) (Figure 5, route b). None of the other reported cationic group 10 metal catalysts tolerate vinyl acetate, vinyl ethers, or acrylonitrile, but BPMO-Pd is observed to tolerate them. However, the origin of the poor reactivity of B (Figure 8) toward ethylene/acrylate copolymerization remains unanswered and challenges our current understanding.

As the substituents on the phosphine-oxide were found to influence the reactivity of B (Figure 8, Jordan and co-workers designed a phosphine-phosphonate ligand system (Figure 6(C)). It was found that cationic phosphine-phosphonate palladium (II) complexes (Figure 9(X)) as well as phosphine-bis (diethyl phosphonate) palladium complexes (Figure 9(Y)) indeed polymerize ethylene, although only low molecular weight linear polyethylene is observed to form. These complexes were also found to be active for the copolymerization of ethylene with functional olefins such as methyl acrylate and acrylic acid. Interestingly, the complex with pendent phosphonate group (Figure 9(Y)), shows twice the activity of the other complex (Figure 9(X)). This behavior was attributed to the strong acceleration of chain transfer by the



**Figure 9.** Cationic phosphine-phosphonate Pd (II) complexes.

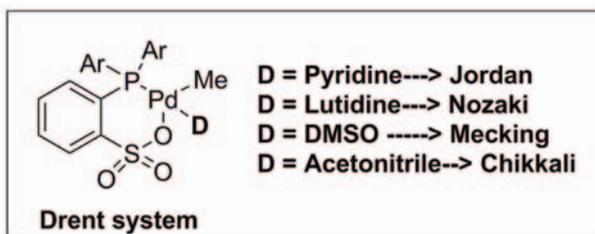


pendant phosphonate moiety.

The structure of PE produced by X (>92%  $\alpha$ -olefin) and Y (>87% internal olefins) (Figure 9) suggests that different chain growth mechanisms are operative in these two catalytic systems. For X, chain growth and chain transfer are fast, and either chain walking is competitive with growth, or the catalyst does not insert ethylene or undergo chain transfer from internal alkyl position to yield linear  $\alpha$ -olefins. Complex Y exhibits fast chain growth and fast chain transfer, but the predominance of internal unsaturation and the absence of branching indicates that chain walking does occur and that the resulting secondary alkyl species undergo chain transfer. The difference in reactivity of these two complexes (X and Y) are again apparent in the copolymerization of ethylene with MA, where X incorporates 1.5 mol% MA, and notably, the MA is selectively (95%) incorporated in-chain. While complex Y gives higher activity and acrylate incorporation (2.6 mol%), it is much less selective than X for in-chain acrylate placement with only 60% incorporated in-chain and 40% incorporated into terminating chain-end groups.

The most successful catalytic system to date has been the neutral, phosphinebenzene sulfonate palladium system invented by Drent *et al.*

The most successful catalytic system to date has been the neutral, phosphinebenzene sulfonate palladium system (Figure 6(D)), invented by Drent *et al.*, [6]. In 2002, Drent reported an *in situ* generated neutral palladium catalyst with a chelating phosphine-sulfonate [ $\text{P}^{\text{A}}\text{O}$ ] ligand and demonstrated that this catalyst is capable of producing a linear copolymer with random incorporation



**Figure 10.** Phosphine-sulfonate palladium complexes with various neutral donor ligands.

Various polar vinyl monomers that have been successfully applied in insertion copolymerization with ethylene include: acrylates, acrylonitrile, acrylamides, acrylic acid, vinyl acetate, vinyl halides, vinyl ethers, allyl monomers, vinyl ketones, and vinyl sulfones.

of functional olefins [7]. These results led to a resurgence in the field of insertion copolymerization of functional vinyl monomers with isolated, neutral, phosphine-sulfonate palladium complexes as catalysts. Encouraged by Drent's early reports, the isolated phosphine-sulfonate palladium catalytic system was investigated thoroughly and was found to tolerate a large variety of functionalities. Various polar vinyl monomers that have been successfully applied in insertion copolymerization with ethylene include: acrylates, acrylonitrile, acrylamides, acrylic acid, vinyl acetate, vinyl halides, vinyl ethers, allyl monomers, vinyl ketones, and vinyl sulfones (*Figure 6(F)*). In all these cases, the polymer produced was highly linear (ca. 1 branch per 1000 backbone carbons), and on an average, 2–10% functional olefin incorporation was observed. The highest incorporation of 52% was observed only in case of MA; however at the expense of low molecular weight. This limitation was addressed by placing bulky substituents on the phosphorus atom, which led to an increase in both the productivity and the molecular weight of the resultant copolymer.

The role of placeholder ligand D in the Drent system was found to extensively influence the catalytic activity (*Figure 10*). The original Drent system was an *in situ* generated, loosely defined palladium complex. However, Jordan and co-workers utilized pyridine as a placeholder ligand and demonstrated insertion copolymerization of alkyl vinyl ethers [8].

The strongly chelating pyridine donor molecule was replaced with lutidine by Nozaki and co-workers, and insertion copolymerization of acrylonitrile was reported [9]. Among the various donor



Olefins that can deliver more functional groups per insertion to the PE backbone would represent a better choice for the manufacture of functional polyethylenes.

groups tested, Mecking and co-workers found that DMSO as a placeholder ligand exhibits the highest productivity ( $26 \text{ gmmol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ ) for copolymerization of ethylene and MA [10]. Going one step further, insertion polymerization of neat MA was attempted, and homo-oligomerization of MA was achieved. The homo-oligomerization was suggested to proceed *via* the coordination-insertion mechanism.

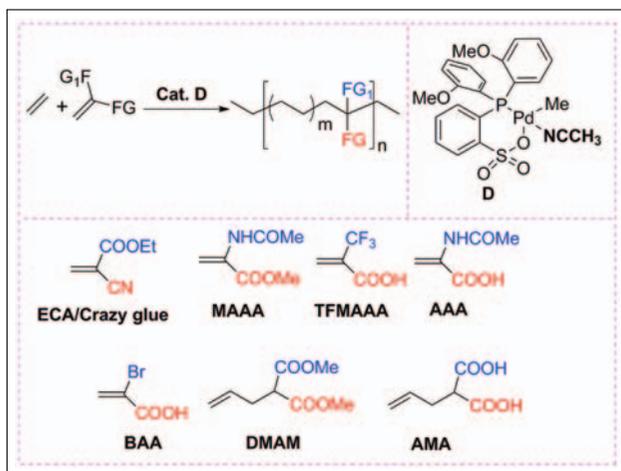
Thus, the primary goal of several of the above reports was to synthesize polyethylene with functional groups installed on the backbone. However, almost every report dealt with mono-functional olefins that yields one functional group per insertion to the polyethylene backbone. In my group, we anticipated that olefins that can deliver more functional groups per insertion to the PE backbone would represent a better choice for the manufacture of functional polyethylenes. Thus, insertion of difunctional monomer would double the functional group density in the resultant copolymer, at a similar percentage incorporation of polar monomer. My group has used acetonitrile as the placeholder ligand and has demonstrated insertion copolymerization of 1,1-disubstituted difunctional olefins for the first time [11].

Difunctional olefins such as ethyl cyanoacrylate are regularly used in instant adhesives such as Fevikwik<sup>®</sup> – a common commercial glue. We have been able to incorporate ethyl cyanoacrylate into the PE backbone, leading to a functional polyethylene. The scope of this invention was extended, and insertion copolymerization of a range of 1,1-disubstituted difunctional olefins with ethylene was demonstrated (*Figure 11*). We have demonstrated an incorporation of 11.8%, which we achieved for dimethyl allyl malonate (DMAM). Although the percentage incorporation might not appear particularly high, remember that each DMAM carries two functional groups. Thus, the functional group density for 11.8% incorporation is an impressive 24%.

<sup>3</sup>Water hating.

Carry bags made up of PE are highly hydrophobic<sup>3</sup> and therefore do not get wet when you dip them in water. Although this feature of PE makes it a useful packaging material for storing goods or wrapping food items, it prevents its use in applications such as





**Figure 11.** Insertion copolymerization of 1,1-disubstituted difunctional olefins catalyzed by acetonitrile ligated complex D (ECA = Ethyl cyanoacrylate, MAAA = Methyl 2-acetamidoacrylate, TFMAA = 2-(trifluoromethyl)acrylic acid, AAA = Acetamidoacrylic acid, BAA = 2-bromoacrylic acid, DMAM = Dimethyl allyl malonate, AMA = Allyl malonic acid).

<sup>4</sup>Water loving.

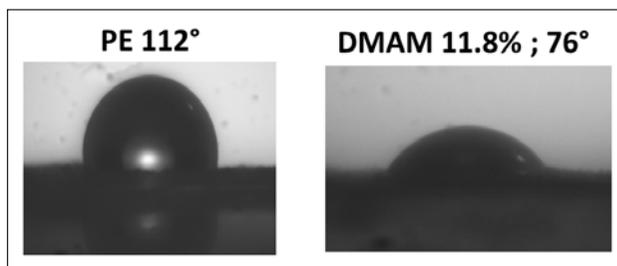
<sup>5</sup>Water contact angle is the angle made by a drop of water placed on a polymer sheet.

glues or adhesives. This limitation of PE can be addressed by incorporating a few hydrophilic<sup>4</sup> functional groups in the PE backbone to drastically alter its physical properties. For example, incorporation of hydrophilic acidic groups would impart increased water loving character to PE. The hydrophilicity or hydrophobicity of PE can be tested by measuring its ‘water contact angle’<sup>5</sup>. Thus, to evaluate the functional PE prepared by the incorporation of 11.8% of DMAM, the water contact angle was measured and was compared with standard water hating PE (*Figure 12*). As it is evident from *Figure 12*, the water contact angle for standard PE was 112°. In contrast, the water contact angle for DMAM functionalized PE was reduced to 76° (±3). These findings clearly show that our strategy to incorporate DMAM has resulted in dramatically increasing the hydrophilicity of PE copolymers relative to pure PE.

Functional olefin copolymerization research has focused on preparing copolymers of ethylene with functional olefins. However, functional olefin copolymerization of another large volume commodity polymer – polypropylene (PP) – is even more challenging and had not been addressed until recently. The lower reactivity of propylene compared to ethylene makes the preparation of propylene-functional olefin copolymers especially daunting. The most recent development in the area of functional olefin

Functional olefin copolymerization of polypropylene is highly challenging and had not been addressed until recently.

**Figure 12.** Water contact angle for pure polyethylene (left) and DMAM functionalized polyethylene (right).



copolymerization addresses this remaining challenge and reports propylene functional olefin copolymerization. Nozaki and co-workers designed imidazoquinoline derived ligand – imidazo[1,5-a]quinolin-9-olate-1-ylidene (IzQO), which upon reacting with palladium precursor yielded a neutral palladium complex E (Figure 6) [12]. The palladium complex was found to initiate the copolymerization of propylene with various functional olefins. The copolymerization revealed a modest 1–2% functional olefin incorporation with copolymer molecular weights in the range of 2000–17000 g/mol. The success of this system lies in the structural confinement of the NHC (NHC = N-hetero cyclic carbene) plane on the metal. The scope of this catalytic system was extended and corresponding nickel complexes Ni/IzQO were prepared [13].

These Ni/IzQO complexes were found to initiate the copolymerization of functional olefins with ethylene. In fact, this is the first successful report on utilizing nickel catalyst in ethylene-functional olefin copolymerization, although the incorporation of functional olefin was limited to 1–2% only.

## 5. Applications

Although a wide variety of polyolefins are commercially available, none of them are functional. Thus, commercial polyolefins do not have properties such as adhesion, miscibility, and printability. The hydrophobic nature of polyolefins makes them unsuitable as binders, coatings, adhesives, paints, primers and so on (Figure 12). Hence, the last two decades have witnessed a growing

Commercial polyolefins do not have properties such as adhesion, miscibility, and printability.



interest in introducing functional groups to the polyolefin backbone to equip them to deliver functions such as enhanced adhesiveness, improved water contact angle, etc. With the insertion copolymerization of functional olefins discussed in the last part of this article, incorporations as high as 17% functional olefins have been achieved. As revealed by the water contact angle measurements, incorporation of functional olefins can lead to enhanced hydrophilicity of the resultant copolymers, and we have obtained water contact angles as low as  $76^\circ$ . This observation supports the hypothesis that introduction of functional groups increases the adhesion and binding properties of the resultant polymeric material. While none of them have been commercialized so far, functional polyolefins hold promise for applications in the following areas:

- 1) As binders in book-binding.
- 2) As glue in adhesives.
- 3) In printing inks.
- 4) As a compatibilizing agent for blends of hydrophilic and hydrophobic polymers.

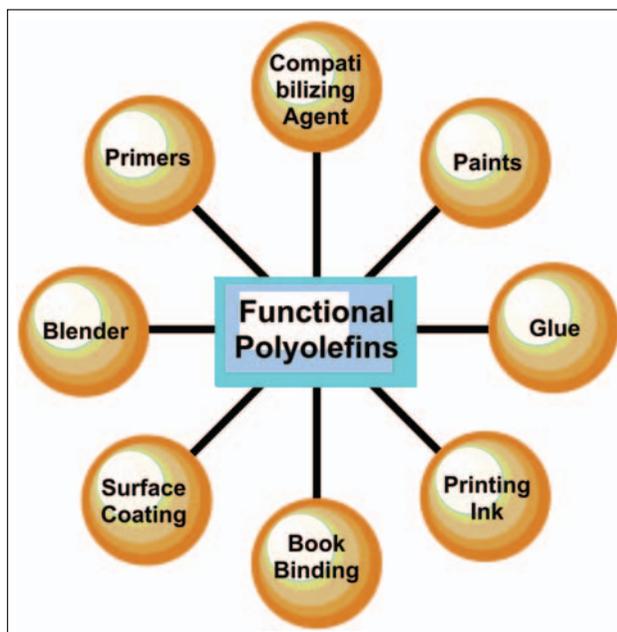
Additionally, they can be used in various applications as presented in *Figure 13*. The intense research interest in functionalized polyolefins is poised to open up the industrial applications of such materials.

To conclude, we cannot imagine life in the 21st century without polymers. Today, almost everything can be, and often is, made from polymers. It is, therefore, amazing that just 100 years ago, a majority of the scientific community did not believe in the existence of polymers. It took almost 30 years for the two Hermans to convince the scientific community that polymers are large molecules and that they do exist. Building on the foundations of this new polymer science, Prof. Karl Ziegler taught us that catalytic polymerization of ethylene using titanium tetrachloride and triethylaluminium would yield an immensely useful polymer – polyethylene. This discovery was immediately recognized as ‘revolutionary in its significance’ by Ziegler’s contemporaries, and indeed, it has revolutionized the field of polymer science.

The intense research interest in functionalized polyolefins is poised to open up the industrial applications of such materials.



**Figure 13.** Potential applications of functional polyolefins.



It remains a significant challenge to produce high molecular weight functionalized polyolefins with a controlled incorporation of functional groups in the polyolefin backbone.

Over the past 70 years, polyolefins have grown to dominate the field of synthetic polymers. Polyolefins serve the society in various forms and have reached every nook and corner of this planet. Despite this seeming maturity, the field of *Z-N*/insertion polymerization continues to surprise us and is as young as ever. The current frontier in this polymerization method is the preparation of functional polyethylenes. To this end, late-transition metal-based catalytic systems A, B, C, D, and E (as shown in *Figure 6*), have been identified as the most successful catalysts. These catalysts enable insertion copolymerization of various functional olefins with ethylene to deliver functionalized PEs. Hydrophobic PEs have been modified by researchers to transform it into hydrophilic functionalized PE.

Despite all this progress, it remains a significant challenge to produce high molecular weight functionalized polyolefins with a controlled incorporation of functional groups in the polyolefin backbone. The remaining challenges that will enable the field of insertion polymerization to reach its full potential are listed below.

1. Achieving high catalytic activity is critical to make functional PEs industrially viable.
2. The molecular weight of the copolymers need to be increased several folds to make them suitable for real-world applications.
3. None of the present catalysts are capable of polymerizing functional olefins to sufficiently high molecular weights. At best, only oligomers can be obtained currently.
4. Even more challenging task is the stereoregular insertion of functional olefins during copolymerization.
5. Although some breakthroughs have been reported, even late transition metal catalysts are susceptible to poisoning *via* functional group coordination or functional group elimination.

In a nutshell, Ziegler–Natta polymerization has evolved significantly beyond the wildest imagination of its founding fathers. Addressing these new challenges will give a new spin to this 70-year-old reaction.

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