

# Catalysts for plastics – New science for new materials

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*The purpose of this article is two-fold. It starts with the premise that, in all probability, the science and technology of the twenty-first century will be far more inter-linked than they have ever been. The article aims to show how critically important oriented basic science has been for the development of the enormously successful manufacturing technologies for polyolefins. These are materials more commonly known as plastics. It also aims to show how the reverse is equally true, i.e. how the demands of technology in turn have propelled and continue to inspire creative academic research. This is one of those clear examples where the paths of science and technology, theory and experiment, discovery and innovation, knowledge and commerce continually criss-cross. An article along these lines, at a time when terms like 'academy industry linkages', the 'knowledge society', etc. are being constantly used, may be of some special value to the Indian scientific community.*

CHEMISTRY is called a 'molecular science'. In practice, among other things, this means that if we knew what the molecules looked like, we could predict more or less precisely how they would behave. This is validated beautifully in the science and technology of polyolefins. A central concept of chemistry, from the time of Kekule till today, has been the concept of a chemical 'bond'. A molecular level structural description of the catalysts used for making polyolefins illustrates the many mysteries of *metal to carbon* bonds. Hopefully for these reasons the article may be of some interest to all chemists, even the purists in the community.

## A historical perspective: The discoveries and the innovations

The story of polyolefins spans more than 50 years and has its origin in the world of mega-industries and pristine academic laboratories. Polyethylene, the most important member of the polyolefin family, was discovered accidentally in the ICI laboratory in 1933. Ethylene in the presence of benzaldehyde was subjected to high temperature and pressure. The waxy material obtained this way was called low density polyethylene (LDPE). In the early 1950s two other industrial laboratories, Standard Oil (Indiana) and Philips Petroleum, reported manufacturing processes of a higher density polyethylene (HDPE). Another major technological breakthrough took place

after more than two decades. A novel process called the Unipol process was reported by Union Carbide for the manufacture of another variant of polyethylene, the so-called linear low density polyethylene (LLDPE), in the late 1970s. Here ethylene is co-polymerized with a small quantity of an  $\alpha$ -olefin, such as 1-octene or 1-butene. As shown in Figure 1, in terms of molecular structures, HDPE has very few branches, LDPE has many, and LLDPE is somewhere in between.

Around the time HDPE was discovered by Standard Oil and Philips Petroleum, Karl Ziegler, then the director of the Max Planck Institute for Coal Research in Mullheim reported a novel reaction of ethylene. He described this reaction as the 'Aufbau' (growth) reaction<sup>1,2</sup>. Ziegler's 'Aufbau' reaction is now of course commonly described as the polymerization reaction. Ziegler also studied the effects of different metals and reported what he called the 'nickel effect' which is now recognized to be a quick termination of the polymer growth. In fact in another highly successful industrial process (Shell higher olefin process), soluble nickel complexes are used to make ethylene oligomers of twenty to thirty carbon atoms.

Ziegler's discovery was soon followed by Giulio Natta's discovery in Italy<sup>3</sup>. Natta reported a catalytic system for making polypropylene of high crystallinity. As shown in Figure 1, the methyl groups in polypropylene can have different relative orientations. Natta realized that isotactic polypropylene, because of its regular molecular structure, had a high crystallinity and was a useful polymeric material. He was able to develop a catalytic system that gave predominantly isotactic polypropylene.

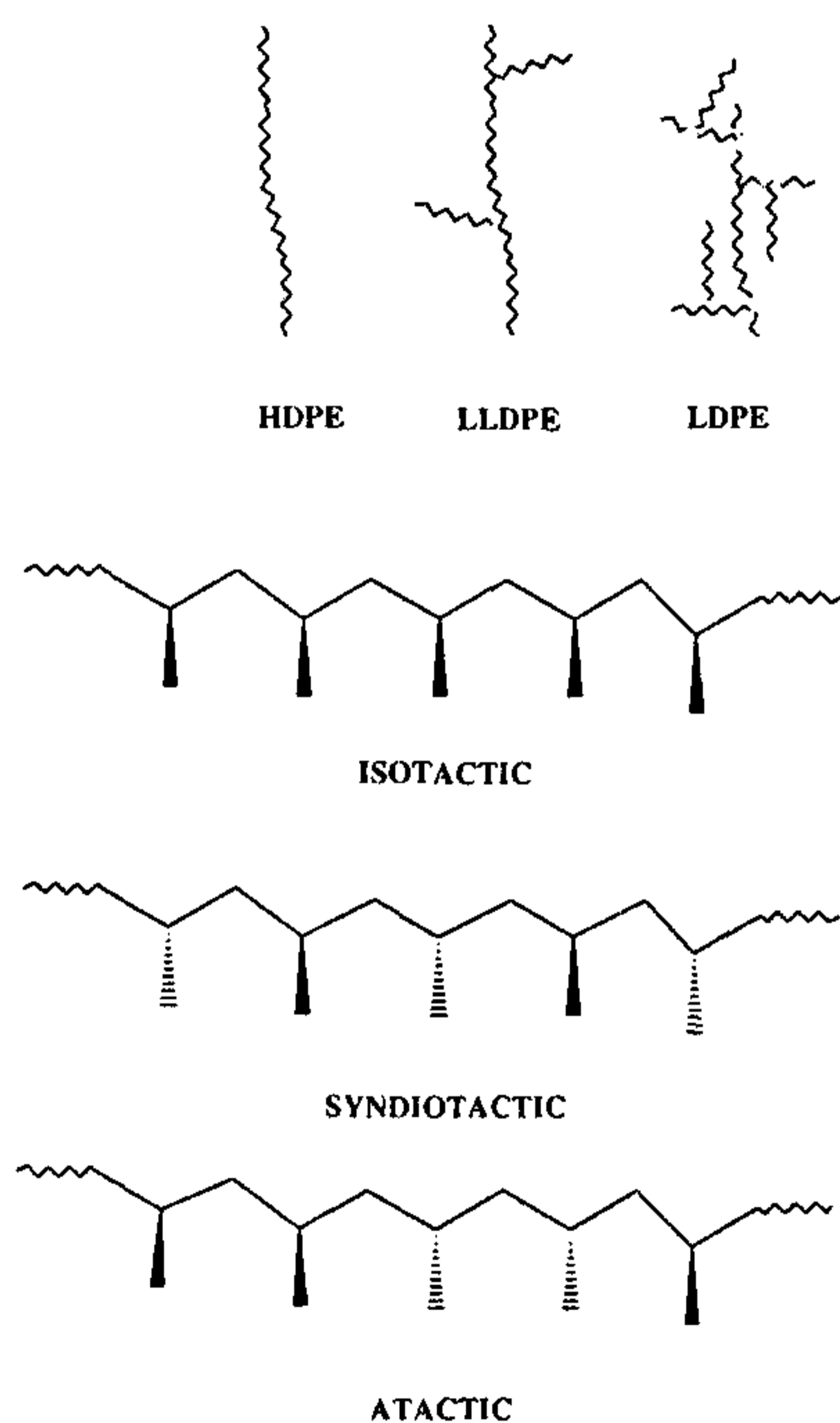
Ziegler and Natta shared the Nobel Prize in 1963, two years before R. B. Woodward and one year before

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Dorothy Hodgkin. In the citation, the Nobel Committee said that they were awarded the prize for 'their discoveries in the field of chemistry and *technology* of high polymers' (*italics added*). This probably is the only time when the word 'technology' found an explicit use in a Nobel citation. Ziegler in his Nobel lecture showed a world map indicating all the large polyethylene manufacturing facilities that were based on his discovery. The time gap between the discovery and the successful worldwide technology adoption was only ten years – a record even by today's standards.

The other interesting point in the present context is the attitude of Ziegler and Natta towards research. Ziegler had accepted the directorship of Kaiser Wilhelm Institute (later known as Max Plank Institute) for Coal Research in Mullheim on condition that he could work on any research project of his choice and not be limited to the chemistry of coal. Natta did his doctorate in chemical engineering rather than chemistry, as he wanted his research to be industrially useful<sup>4</sup>. His work, subsidized by Montecatini Company in Milan, involved among other things the use of X-ray and electron diffraction, highly sophisticated physical techniques of that time. This apparently esoteric work was, nonetheless, carried out in the Industrial Chemical Research Center of the Milan Polytechnic Institute.



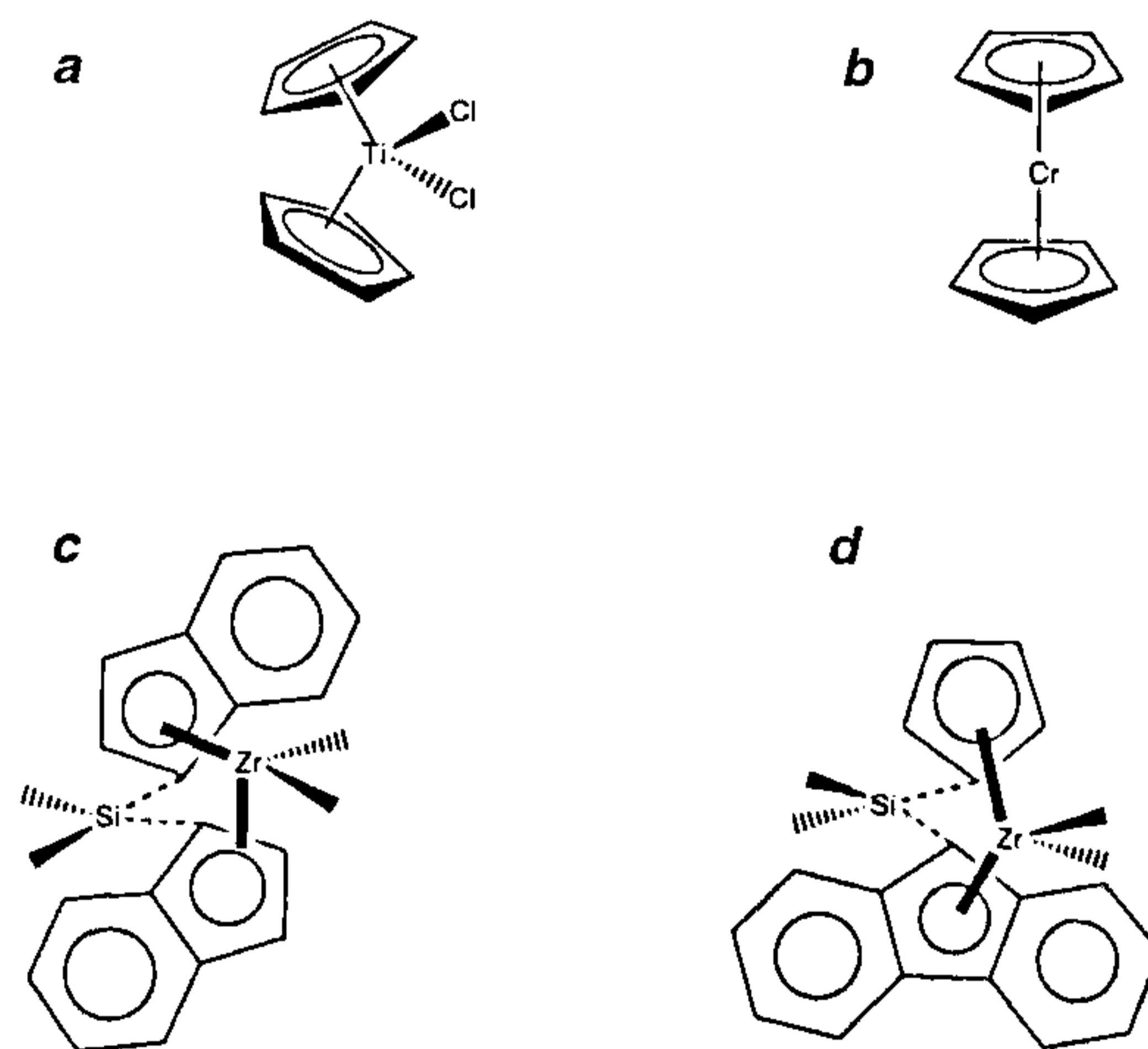
**Figure 1.** Schematic presentations of polymer molecules of different types of polyethylene (upper left) and polypropylene. In isotactic and atactic polypropylene the orientations of the methyl groups, with respect to the polymer chain, are all in the same direction and random respectively. In syndiotactic polypropylene every alternate methyl group has the same orientation.

In the early 1950s, while these exciting developments took place in the laboratories of Ziegler and Natta, another novel class of compounds, known as 'sandwich' complexes, were reported<sup>5-7</sup>. Two of the scientists, Wilkinson and Fischer, shared the Nobel Prize in 1973 for their pioneering work in this area. These sandwich complexes, typical examples of which are shown in Figure 2, are also known as *metallocenes*. They played a pivotal role in the subsequent growth and development of the organometallic chemistry of the transition elements. In the present context what is especially noteworthy is that in the 1990s metallocenes have emerged as the future industrial catalysts for polyolefins. Their origin however, like most important discoveries in science, was firmly rooted in pure curiosity-driven creativity that did not have any application whatsoever in mind. The basic question that Wilkinson, Fischer and others tried to answer dealt with the nature of the metal-carbon bond.

It is also interesting to note that, metallocenes did find an early, though limited, industrial application. A conventional *solid* catalyst for the manufacture of polyethylene is made by reacting chromocene with silica. However, as we will see, the present generation of *soluble* metallocene catalysts is qualitatively different from this early catalyst and is in a class by itself.

### The 'market-pull' and 'technology-push' of the polyolefin industry

A generally accepted truism of research management is based on the 'push-pull' concept of organic reaction



**Figure 2.** Examples of metallocene or 'sandwich' complexes. Strictly speaking chromocene (top right) is the only real 'sandwich' complex as it has a chromium atom sandwiched between two identical planar cyclopentadiene rings. Chromocene was used to make one of the early industrial catalysts by reacting it with silica. The two complexes at the bottom are recent metallocene catalysts. The one to the left has a  $C_2$  symmetry axis and is chiral. It gives highly isotactic polypropylene. The one to the right has a plane of symmetry and gives highly syndiotactic polypropylene.

mechanisms<sup>8</sup>. Basically, it is thought that the successful commercialization of any new science is rapid and smooth only if there is a good synergy between the market-pull and the technology-push. This is clearly exemplified in the progressive improvements that have taken place over the last five decades in the polyolefin technology. The technologies of polyethylene and polypropylene manufacture, and the underlying science that makes it possible, have come a long way from that of the original Ziegler–Natta discoveries.

The technological and commercial importance of these two leading members of the polyolefin family could be partly gauged from the global production figures. In 1997 total global production of polyolefin was approximately 75 million metric tons, and by the year 2015, the production of only polyethylene is projected to be of the order of 150 million metric tons<sup>9</sup>. The reason for this spectacular growth is primarily because of the enormous versatility of polyolefins, especially polyethylene and polypropylene, in terms of applications and economic processing. These are the ‘market-pulls’ that make new technology an essential component in the overall competitiveness of all large petrochemical industries. Second, molecular tailoring of the catalysts and innovative down stream processing provides the ‘technology-push’ that vastly extends the application horizon of these materials.

The crucial and probably the most important links in the innovation chains of all polyolefin technologies are the catalysts. From the time of Ziegler and Natta’s original discovery, catalyst systems have undergone tremendous improvements. A standard reference book on chemical technology lists five distinct generations of catalysts with progressive and clear improvements over the previous generation<sup>10</sup>. To keep the discussion focused on how a molecular level understanding has led to these developments, we classify the catalyst systems in the following three categories:

1. Original Ziegler–Natta type systems which could be colloidal or solid catalysts. In this article we classify these as the first generation catalysts.
2. Solid catalysts consisting of magnesium chloride supported titanium chloride, and used in combination with additives. These we classify as the second generation catalysts.
3. Metal sandwich complexes or metallocenes.

In the rest of this article we concentrate on scientific findings that made the ‘technology-push’ a powerful and incessant one. In other words, we try to highlight how conceptual sophistication backed by hard scientific data, and technological improvements on a plant scale, have progressed hand in hand.

### Evolution of the catalysts

The discovery and investigations of the first generation catalytic systems fairly soon led to the following conclu-

sions: (1) A combination of titanium tetrachloride and an alkyl aluminum reagent (usually triethyl aluminium or diethyl aluminum chloride) gives a highly active polymerization catalyst for both ethylene and propylene. (2) The relative orientations of the methyl groups in polypropylene could be correlated to the solid state structures of the titanium trichloride crystals. The selectivity towards isotactic polypropylene is more if the crystal morphology is the right one. (3) In the case of propylene polymerization, additives like ethers, esters, etc. influence the activity and the selectivity of the catalyst.

Starting with the discovery of the sandwich complexes, academic organometallic chemistry in the next three decades made impressive progress in the rational synthesis, the elucidation of structure, and the explanation of observed reactivity of compounds with metal–carbon bonds. This was also the period when industrial laboratories achieved dramatic improvements in polyolefin manufacturing facilities both in terms of catalyst activity and reaction engineering<sup>11–13</sup>. This is the period that we have loosely classified as the phase of the second-generation catalysts.

The basic catalyst system of the second-generation catalysts consists of titanium chloride supported on magnesium chloride. The catalyst must be used in combination with an organoaluminum reagent. Additives such as phthalate esters or silicon atom containing diethers, commonly called ‘electron donors’, must be added for highly isotactic polypropylene. The inventions that relate to catalyst improvements both in terms of activity and selectivity have been the subject matter of many patents. However very little hard scientific data, that involves the use of sophisticated techniques for the study of solid surfaces, have been reported in the open literature.

This is not surprising for three reasons. First, industry will be happy as long as something works well, day in and day out, in a reproducible and predictable manner. Secondly, assuming that hard data is available, industry may not be keen to publish such data as open literature and make it available to the competitors. Thirdly (probably the most important reason is that) molecular level structural studies of the surface species of a highly air and moisture sensitive active catalyst is a difficult research problem even today. It is worth remembering that the plethora of surface microscopic and other techniques that may provide molecular level structural information is of fairly recent vintage, and not routinely available to or mastered by most synthetic chemists.

The third generation of catalysts belongs to the class of ‘sandwich complexes’. While industry was busy perfecting the manufacturing process, a serendipitous innovation in the laboratory of Kaminsky at Hamburg paved the way for the technological exploitation of metallocenes as catalysts<sup>14</sup>. It was found that small quantities of water turned a mixture of  $\text{Cp}_2\text{TiCl}_2$  (Figure 2) and  $\text{Me}_3\text{Al}$  into an active catalyst for the polymerization of olefins. Both industry and academia vigorously followed up this initial report.

At a rough estimate, by the year 2003, at least 5% of the total global production of polypropylene (approximately half a million metric ton) is expected to be based on metallocene catalysts. Apart from polypropylene, metallocene catalysts are being used for making a variety of specialty polymers. This is because unlike the catalysts of the previous generations, metallocenes can polymerize a very wide range of alkenes and mixtures of alkenes<sup>15,16</sup>. The polymers obtained by using metallocene catalysts also have a very narrow range of molecular weight distribution. Most importantly, with these catalysts the tacticity of the polymers can be controlled with high precision. We now discuss the mechanistic and structural details of the catalysts at a molecular level. For the metallocene catalysts such a description ties up beautifully with the structural details of the resultant polymer molecule.

### Molecules and mechanisms

The basic questions that must be addressed are as follows.

1. What is the fundamental difference between the three generations of catalysts at a molecular level?
2. Since polymer formation means the formation of new carbon to carbon bonds, what role does the metal play in that?
3. If the formation of a metal to carbon bond is involved at any stage of the mechanism, what sort of a bond is it? In other words, is it a single bond or a double bond or not quite a bond, but an interaction?
4. Why was it necessary to have trace quantities of water for the metallocene catalysts activated with trimethyl aluminum?
5. How is it possible to control the molecular structures of the resultant polymer molecules by tinkering with the molecular structures of the catalysts?

The first question deals with the difference between *homogeneous* and *heterogeneous* catalysts. The second-generation catalysts, i.e.  $\text{TiCl}_4$  with or without other additives supported on  $\text{MgCl}_2$  are *heterogeneous* catalysts. The coordination environments around the titanium ions on the surface are not identical. Many such environments are possible and are actually present. Of these various molecular structures and environments only a few will be catalytically active. These are called the active sites. Even within the class of active sites there are structural and environmental differences. The titanium ions may be at the edge of the crystal, or at the corner, or may have different numbers of anion vacancies around them and so on. Because of this inequivalence the polymer molecules that grow on each of these sites need not have identical structure, length, and molecular weight.

Although Ziegler catalysts are often made in an organic solvent by the treatment of  $\text{TiCl}_4$  with trialkylaluminum, in terms of molecular level structures they are similar to

the heterogeneous catalysts. This is because these are colloidal systems and the molecular structures and environments at and around the titanium ions on the surface of these colloidal assemblies are obviously not identical.

Unlike the first and second generation catalysts, metallocenes are *homogeneous* catalysts. For a given metallocene catalyst, all molecules have the same structure and behave in an identical manner. Therefore the polymer molecules that grow on each of these sites (molecules) should have nearly identical structure and molecular weight. This in fact is what is observed in practice. Consequently the metallocene catalysts are often referred to as *single site* catalysts.

The answers to the second and third questions are based on some of the fundamental and recent concepts of organometallic chemistry. It may be worth remembering that the direct evidence for any sort of a bond in most cases is based on single crystal X-ray study, a technique that became more or less routine only in the early 1970s. During the development of the first generation catalysts it was clear that, among the first row transition metals, titanium showed maximum polymerization activity. Good polymerization activity was also observed with other early transition metals such as vanadium and chromium.

Although the formal charge on the titanium ion at the active site, was assumed to be 4+, direct evidence was not available. Indeed until the early 1980s there was some speculation on whether or not paramagnetic metal ions (e.g.  $\text{Ti}^{3+}$ ) have a special role to play in the polymerization process. Some elegant and careful work in Du Pont and other laboratories showed that paramagnetic metal ions do not have any special role<sup>17</sup>. Such work also provided direct spectroscopic evidence for all the proposed mechanistic steps of a polymerization reaction. A simplified mechanistic scheme, which is based on standard well-established organometallic reactions, is shown in Figure 3. Here it should be mentioned that recent studies<sup>18</sup> also suggest that in the commercial silica supported chromocene-derived catalyst the active sites are most probably  $\text{Cr}^{3+}$  rather than  $\text{Cr}^{2+}$ .

As already mentioned, sophisticated spectroscopic and microscopic studies on  $\text{MgCl}_2$  supported  $\text{TiCl}_4$  plus additive based active catalytic systems, have not been reported in the open literature. Cossee and Arlman proposed the original mechanism of polymerization with the first generation catalysts<sup>19</sup>. The mechanistic scheme is virtually the same as that shown in Figure 3. The important point is that the formation of the new carbon to carbon bond was assumed to involve *direct* insertion of the olefin into the metal-carbon bond.

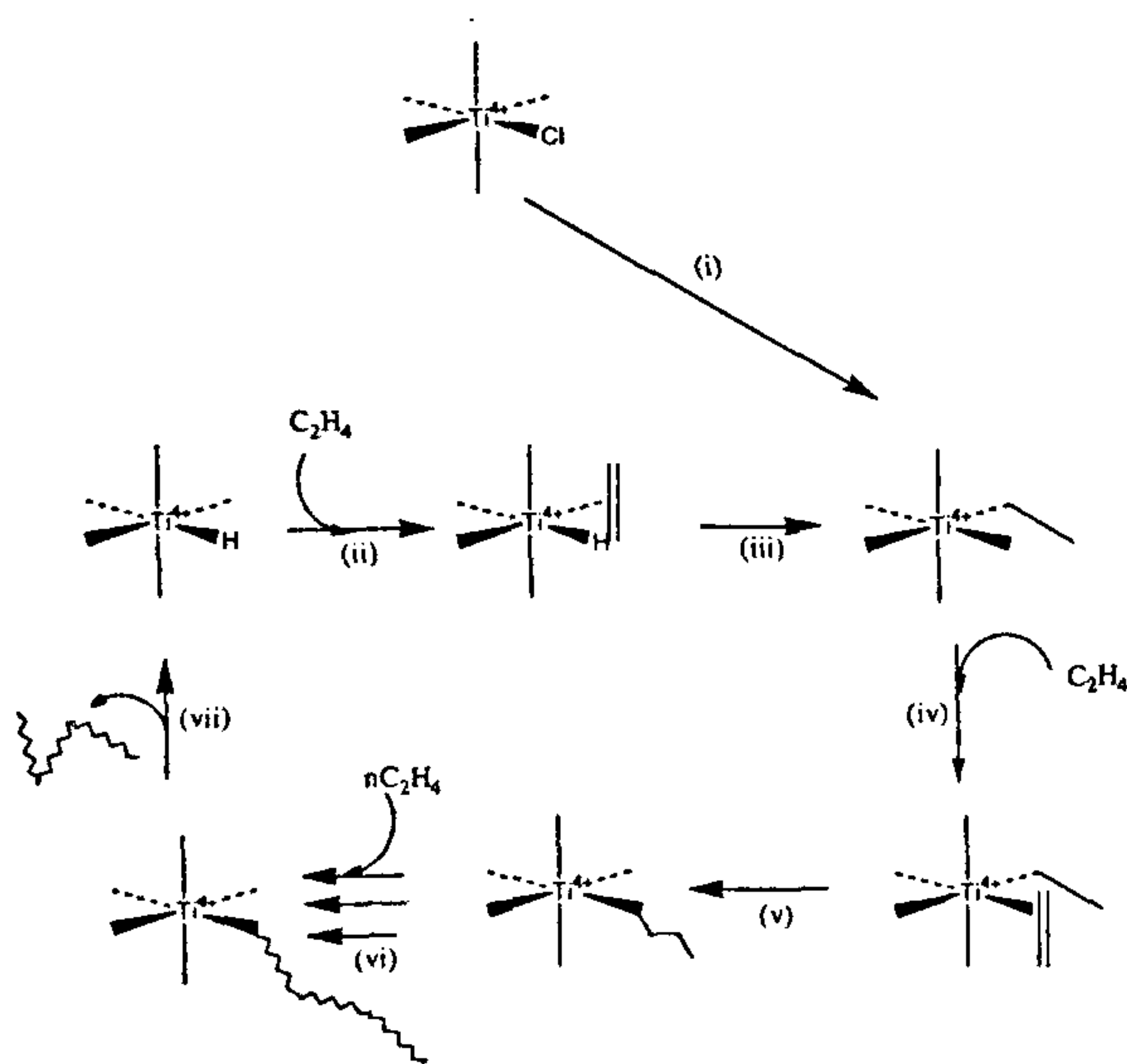
Propylene and ethylene are both planar molecules. Unlike ethylene, in propylene the two faces of the plane have opposite handedness. In chemical terminology this is called a 'prochiral molecule'. Cossee and Arlman also proposed that for isotactic polypropylene, the titanium centres where the polymer chain grew were accessible to

propylene only if it approached the metal centre through one particular face. In other words the coordination environment around titanium had an in-built asymmetry that led to isotacticity.

We mentioned earlier that addition of various bases or the so-called 'electron donors' has a beneficial effect on the stereoregularity of polypropylene. On the basis of kinetic analysis, it is by and large agreed that the 'donors' coordinate to the more active but less selective sites. This increases the isotacticity of the polymer but often at the cost of the overall rate of polymerization.

During the 1970s and 1980s, academic research tried to integrate the mechanism of polymerization with the rapidly advancing frontiers of organometallic chemistry. The evidences for the existence of an intermediate with a metal to carbon *single* bond were many. A large number of transition metal alkyl complexes were synthesized and structurally characterized. One of them reported by Wilkinson in the early 1970s is shown in Figure 4 (structure 4.1).

The chemistry of complexes with metal to carbon *double* bonds, the so-called metal-carbene complexes<sup>20</sup>, was also fully developed by Fischer (structure 4.2, Figure 4). Instead of the Cossee-Arlman mechanism that involves metal-alkyl intermediates, an alternative mechanism involving a carbene intermediate was proposed by Green *et al.*<sup>21</sup>. Carefully-designed experiments to differentiate between these two mechanisms by using isotopically labelled compounds were subsequently reported by others. No evidence was found for discrete metal-carbene type intermediates.

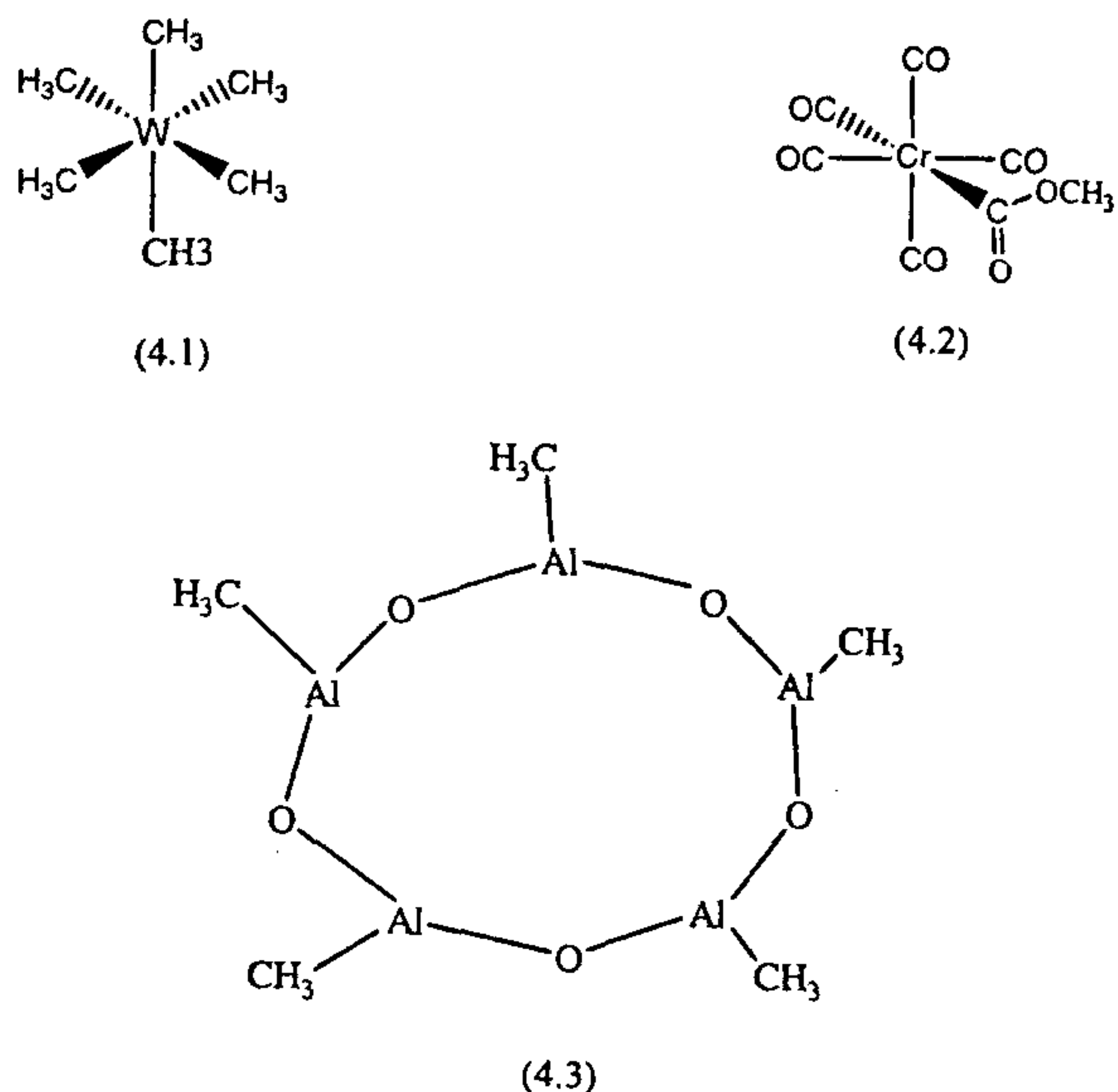


**Figure 3.** Ethylene polymerization according to Cossee-Arlman mechanism. The formations of new C-C bonds as shown for step (v) is thought to be direct (no intermediates). In step (i) the  $\text{Et}_3\text{Al}$  or  $\text{Et}_2\text{AlCl}$  converts the chloride precursor to a titanium ethyl species.

At present, on the basis of a variety of studies that include single crystal X-ray, multinuclear NMR, kinetic isotope effects, theoretical calculations, etc. we have a reasonably clear molecular level understanding of the mechanism<sup>16,22,23</sup>. As mentioned earlier, the metal to carbon bond is a standard metal to alkyl single bond, and the polymer chain grows by the continuous insertion of the olefin into the metal-carbon bond. Furthermore, a short-lived *interaction* between the metal and the hydrogen atom attached to the carbon nearest to the metal, the  $\alpha$  carbon, seems to be important for the tacticity of polypropylene. In the case of polyethylene such an interaction may or may not be present and does not have any practical consequence.

This interaction where the hydrogen atom flirts with the metal atom but does not divorce the carbon and marry the metal is called an 'agostic' (a Greek word) interaction. It has been observed by X-ray and NMR in a large number of organometallic complexes. The currently accepted mechanism for propylene polymerization with metallocene complexes is shown in Figure 5. The basic idea is that in the *transition state* an agostic interaction prevents the rotation around the metal-carbon bond. In this way the relative stereochemical arrangements of the methyl groups in the polypropylene chain are retained.

The answer to question number 4 mentioned earlier is that partial hydrolysis of methyl aluminum generates a mixture of compounds. All these compounds contain



**Figure 4.** Hexamethyl tungsten (4.1) is the first all alkyl transition metal complex made by Wilkinson with all metal to carbon single bonds. The Fischer carbene complex (4.2) is the first of its kind with chromium to carbon double bond. To retain tetravalent carbon, the metal to carbon double bond is formally not shown but the bond distance is indicative of such a bond. Structure 4.3 is one of the early MAO molecules characterized by mass spectrometry.

methyl groups and many Al–O–Al bonds. These compounds are called methyl aluminoxanes (MAO). The suggested structure of one of the many possible MAO molecules is shown by structure 4.3 in Figure 4. The role of MAO is to pull away a methyl group from the metal centre so that there is room for an olefin to come and bond to the metal. This after all is one of the essential requirements for polymerization. In other words MAO produces what in the homogeneous catalysis parlance is called coordinative unsaturation. The sequence of reactions that lead to polymerization is shown in Figure 5.

The answer to the last question is obviously of tremendous practical importance. A large number of sandwich complexes of titanium and zirconium have been found to be efficient polymerization catalysts. The good catalytic activity of the zirconium complexes is not surprising. After all titanium and zirconium belong to the same group in the periodic table. What olefin and how efficiently it may be polymerized would obviously depend on the specific ligand environment used in the metal complex.

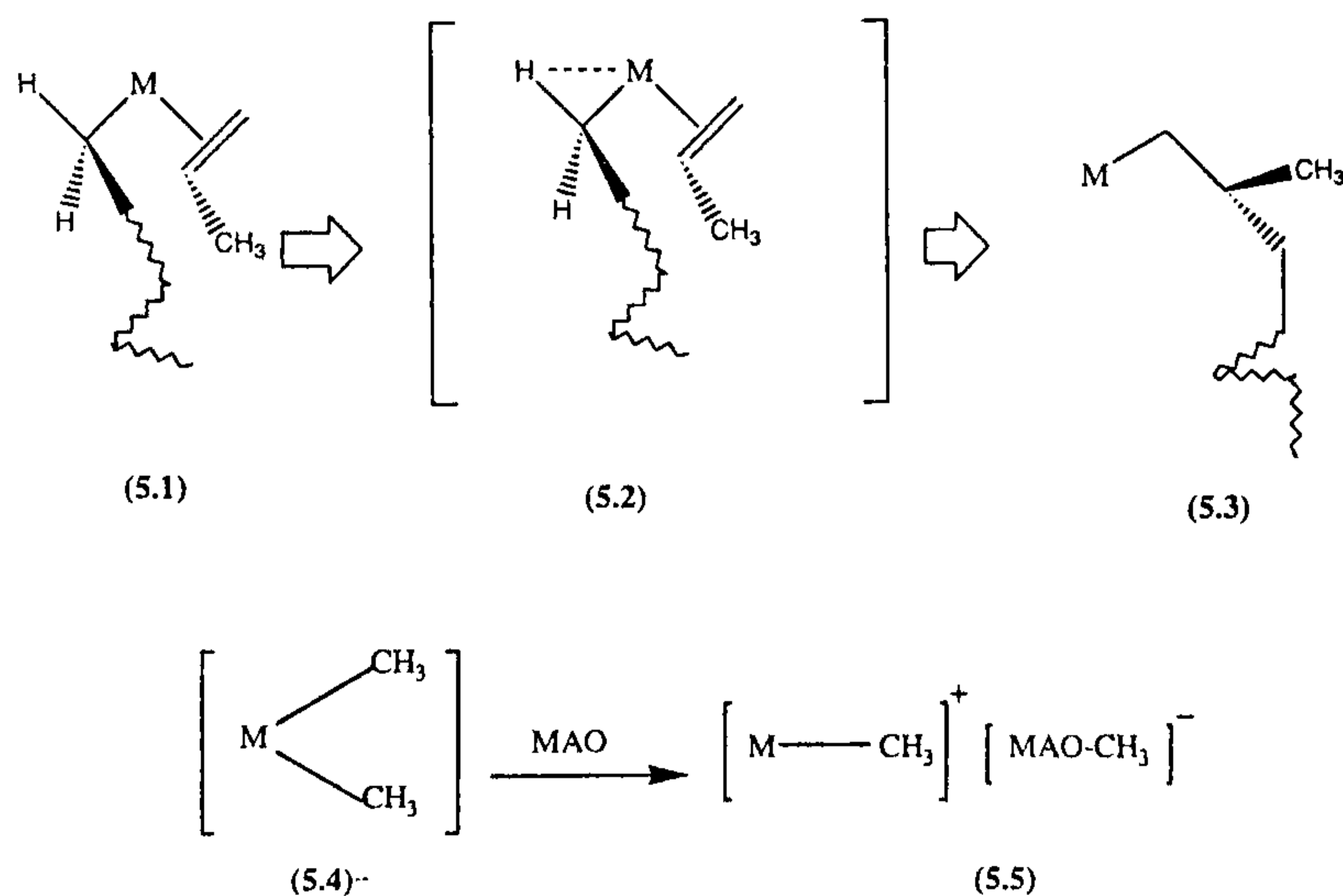
Like many fundamental chemical properties, the symmetry of the catalyst molecule, or more precisely the point group to which the catalyst molecule belongs, has turned out to be the controlling factor in determining the tacticity of polypropylene. Thus by using molecules that are very similar but have different symmetries as catalysts (see structures 2 *c* and *d*) *isotactic* and *syndiotactic* polypropylene could be made in a predictable manner. Chemists would recognize that structures 2 *c* and *d* belong to  $C_2$  and  $C_s$  point groups, respectively.

The space available near the metal forces the growing polymer chain and the methyl group of each incoming propylene molecule to adopt a specific relative position. As already mentioned, due to agostic interaction, rotation around the metal to carbon bond is prevented, i.e. the specific relative position of methyl and the polymer chain is retained. In situations where the path of approach of the olefin to the metal centre cannot be random basically because of the bulk of the ligand, symmetry considerations predict that  $C_2$  and  $C_s$  symmetry should lead to the formation of isotactic and syndiotactic polymers. This indeed is what is observed in practice. A simple but aesthetically pleasing and practically useful correlation indeed<sup>16,24</sup>.

The other major finding is very recent and truly exciting<sup>9,25</sup>. It has been reported that many other ligand and metal combinations, and *not necessarily only sandwich type complexes of titanium or zirconium*, may do the job. What is required is that the ligand forms more than one bond with the metal ion, i.e. it acts as a bi- or tridentate chelate, and is reasonably bulky. An optimum bulk of the ligand is very important for best activity. With these easily synthesized ligands, a cheap innocuous metal like iron gives a very efficient catalyst for the polymerization of ethylene. Like the metallocene catalysts these catalysts are also activated with MAO, and the basic chemistry of polymerization remains the same.

### The future and unanswered questions

There is no doubt that metallocenes and similar catalysts will be increasingly used for making special tailor-made



**Figure 5.** Currently accepted mechanism of polymerization with metallocene catalysts. (Top) Control of tacticity; and (bottom) generation of co-ordinative unsaturation by MAO. The relative *trans* orientation of the methyl group and the growing polymer chain in 5.1 is retained in the transition state 5.2 due to agostic interaction. A broken line represents the agostic interaction between the metal atom and the hydrogen. One of the methyl groups of 5.4 is abstracted by MAO to give the weakly bound ion-pair (5.5). The other ligands on the metal are not shown for clarity.

polymers. However, there are many reasons that make total replacement of the second generation catalysts by metallocenes unlikely in the foreseeable future. There are two chemistry-related issues that may be of special interest to the readers. First of all, for polyethylene and polypropylene, the activities of these new catalysts must be significantly greater than that of the conventional catalysts. Otherwise any plant or hardware modification would obviously be uneconomical.

Many approaches have been adopted to home in on the optimum ligand environment that gives best activity. Potentially a promising one is the so-called 'combinatorial approach' reported by Symx technologies where multiple ligand environments can be simultaneously and quickly evaluated<sup>26</sup>. It is interesting to note that a 'combinatorial approach' was originally reported for solid phase peptide synthesis in the area of pharmaceutical research. The second problem with the new generation catalysts is that these catalysts are activated only in the presence of rather large quantities of MAO. A less expensive and effective way of activating these catalysts is required. While a fair amount of success has been achieved in finding other molecules that do the same job as MAO at a much lower concentration, more needs to be done.

In the Indian context the following long-term techno-commercial trends are certain to prevail. The yearly rate of growth in polyolefin consumption in India, shows a robust 'market-pull' for existing and new technology. The demand for new technology will also become urgent as, with globalization and a level playing field, the market for tailor-made special polymers and differentiated products within the country grows.

This presents many opportunities to academic researchers. The possibility of developing new ligand systems, the applications of computational chemistry and sophisticated surface techniques are some of the most obvious directions. As we have seen with the commercial second generation solid catalysts, very little structural information at a molecular level is available. The explanation of the very important roles played by the additives still remains in the realm of hand-waiving arguments and educated conjectures. Unravelling their mysteries no doubt presents difficult research problems. Only a creative multidisciplinary approach may provide answers to some of the 'know why' questions. The traditional boundaries between the different branches of chemistry, and between

chemistry and materials science must be crossed if we want our contributions to be recognized and rewarded at the international level.

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