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Recent Developments in Ziegler-Natta Catalysts for Olefin Polymerization and Their Processes

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The chemistry of Ziegler-Natta catalysts in olefin polymerization is reviewed. Factors determining catalyst activity are identified for the current generation of high activity - high selectivity catalysts. These include the nature of transition metal, its oxidation states and the ligands around it, the nature of alkylaluminium compounds, the physical state of the catalyst and its dependence on the method of preparation as well as activation of support and the role of internal and external donors. The effect of reaction parameters on catalyst performance as well as effect of nature of catalysts on polymer properties such as molecular weight, molecular weight distribution and stereoregularity are discussed. Current developments in soluble titanium/zirconium, vanadium and magnesium-titanium catalysts are reviewed. Different classes of industrial processes for production of polyethylene and polypropylene, namely slurry phase, gas phase and solution processes are discussed. The nature of contemporary catalysts is exemplified by selected patents from current literature. The various reactor types for polyolefins and salient reactor design aspects are discussed. The dependence of polymer properties on reactor design as well as kinetic modelling and simulation of polyolefin processes are briefly reviewed.

1. Introduction

Polyolefins are a group of bulk commodity polymers comprising of polyethylenes, polypropylene, poly (butene-1) and various copolymers of ethylene, propylene and higher alpha olefins. By volume used, polyolefins are the leading polymers for many applications such as plastics, fibres, films and elastomers. Since their introduction in the early fifties, the polyolefin group of polymers have witnessed unprecedented growth with the result that they have established a niche for themselves in every conceivable area of polymer applications.

1.1 Historical overview

Polyolefins entered the commercial market with the discovery of high pressure low density polyethylene by Fawcett and Gibson in the laboratories of Imperial Chemical Industries in 1934. With the increased availability of ethylene in the early fifties, low density polyethylene came into rapid prominence[1]. Around 1955, Ziegler and his colleagues discovered a revolutionary new chemistry which enabled polymerization of ethylene at very low pressures and temperatures[2]. Under these conditions, it was soon realized that the polyethylene produced had different properties from that of high pressure low density polyethylene. The "Ziegler" polyethylene had a linear structure with very little chain branching. In 1957, the Ziegler process for polyethylene was extended to the polymerization of propylene by Natta in Italy[3]. He made the dramatic discovery that not only propylene could be polymerized to high molecular weight polymers by Ziegler catalysts but the polymer so produced had a highly stereoregular structure (termed isotactic)resulting in improved physical properties. Montecatni Edison under exclusive license from Natta, began commercial manufacture of polypropylene in 1957 in Italy.

The revolutionary discovery of Ziegler and Natta for the polymerization of ethylene and propylene was extended by others to produce polymers from a variety of other monomers such as dienes, cyclic olefins and higher alpha olefins, leading to a large number of polymers and copolymers with an endless array of properties. In view of the fact that they were based on primary and therefore less expensive petrochemical feedstocks, they captured the commodity markets. The estimated world production of polyolefins was approximately 40 million tons in 1985[4].

The polyolefin field has maintained its vigorous growth on account of rapidly improving technology for process and products. In spite of thirty years of existence in the commercial markets, the area is being subjected to frequent technological upheavels. This is schematically illustrated for polyethylene and polypropylene in Fig. 1.

1.2 Scope of Ziegler-Natta catalysts

Ziegler-Natta catalyst as defined in patent descriptions is a mixture of base metal alkyl of group I to III metals and transition metal salt of group IV to VIII metals[5]. The most commonly used transition metal

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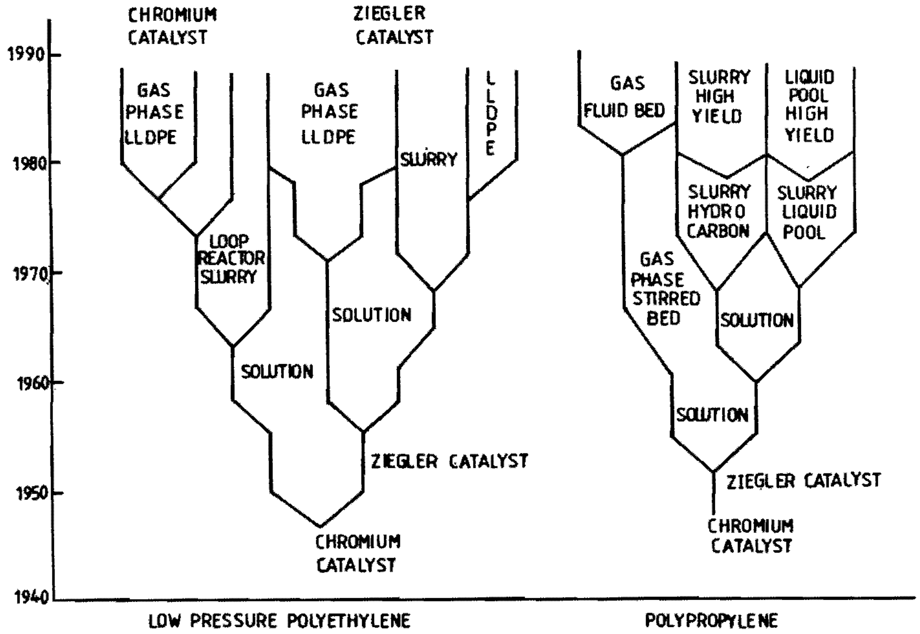


Fig. 1 — Progress tree of polyethylene and polypropylene technology

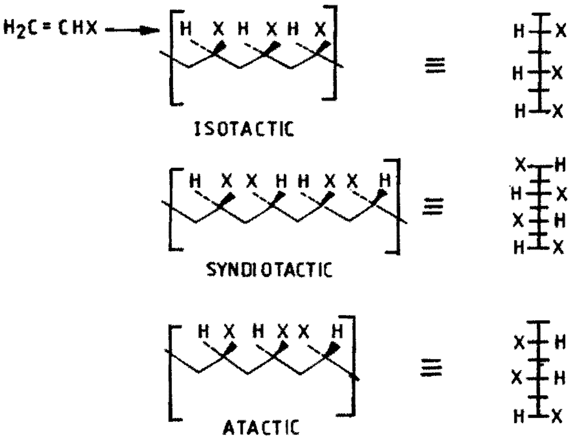


Fig. 2 — Confiuration of isotactic, syndiotactic and atactic polyproplenes

salts are halides and alkoxides of Ti, V, Cr, Co and Ni salts. Organometallic compounds of aluminium are the preferred cocatalysts. Using these class of catalysts a wide variety of acyclic olefins, dienes, cyclic olefins and vinyl monomers have been polymerized and copolymerized to products with useful properties and substantial commercial interest.

The distinctive feature of the Ziegler-Natta catalyst is its extraordinary stereospecificity. Unlike ethylene, which is achiral, propylene is prochiral and therefore upon polymerization can give two distinct configurations, namely isotactic and syndiotactic, depending on the position of the methyl group (Fig.2)[6]. Ziegler-Natta catalysts are highly specific in the sense that they produce exclusively either one or the other configuration depending on the nature of the catalysts.

Table 1—Chronology of Development in Ziegler-Natta Catalysts

	Polyethylene		Polyethylene		
Year	Catalyst	Yield kg/g Ti	Catalyst	Yield kg/g Ti	I.I. %
1953-55	$TiCl_4$+Et_3Al	10-15	$TiCl_3$+Et_2AlCl	1-3	90
1960	—	—	$TiCl_3$+Et_2AlCl+ Electron donor	1-10	92
1975 to present	Supported $TiCl_4$+Et_3Al	1000	Supported Ti+Et_3Al+ Electron donor	300	96

Et_3Al: Triethylaluminium; Et_2AlCl: Diethylaluminium chloride

Beginning early seventies, Ziegler-Natta catalysts underwent revolutionary modifications, whereby high activity catalysts requiring no catalyst removal from polymer appeared on the scene. Table 1 shows a chronology of development for polyolefin catalysts. Rapid developments in propylene catalysts further improved catalyst performance as shown in Table 2[7].

A number of recent reviews[8-18] and a monograph[19] provide extensive coverage of the chemistry of Ziegler-Natta catalyst systems.

1.3 Commercial development of processes

Subsequent to the initial discovery of Ziegler-Natta catalysts, many processes were developed to exploit the catalysts for the commercial manufacture of polyolefins. Initially slurry and solution phase processes were developed, and later processes operating in gas phase or in low boiling diluents came into prominence.

Table 2 — Relative Performance of High Activity Catalysts for Propylene Polymerization[a]

	$TiCl_3$+ Et_2AlCl	High activity catalysts introduced during	
		1975-80	1980-todate
Catalyst productivity, kg PP/g Ti	3	300	300
Catalyst productivity, kg PP/g catalyst	0.3	5	> 12.5
I.I. of polymer, %	90	92	94-98
Bulk density of polymer, g/mL	0.2-0.3	0.5-0.54	0.50-0.54
Flowability, s	25-30	16-20	13-16

[a]Slurry process in heptane: 70°C and 7 kg/cm^2; see Ref. 7.

An important aspect of the current stage of developement of polyolefin processes is that they appear to have almost reached the end point in terms of process engineering. Large single line capacities and simplified processes have reduced to bare minimum the capital and utility costs. Further simplification such as elimination of extrusion, pelletization is already a reality in case of polyethylene and appears imminent for polypropylene also. Target characteristics of catalysts required to produce high bulk density polymers in spherical form with sufficient porosity for absorption of stabilizers and additives have been defined and appear close to commercial availability[20].

1.4 Scope of the review

In spite of three decades of existence, Ziegler-Natta catalysts and processes continue to be the object of innumerable studies in both industrial and academic laboratories. This paper reviews the current understanding of the chemistry behind the new generation of catalysts and its impact on polyolefin process technology. Non-Ziegler systems such as CrO_3/silica are not covered. A brief account of the reaction engineering aspect is also included.

2. Chemistry of Ziegler-Natta Catalysts

2.1 Classification

Ziegler-Natta catalysts can be broadly classified into homogeneous and heterogeneous systems, the physical state referring only to the catalyst and not to the polymer. In the heterogeneous system the catalyst is in a dispersed phase coexisting with a liquid phase and the polymerization occurs mainly on the surface of the solid phase; that is, the reaction loci are situated on the solid phase. One can differentiate two types of catalyst in a heterogeneous system. The transition metal salt can be a pure solid compound such as titanium trichloride ($TiCl_3$), vanadium trichloride or an alloy with a metal halide, e.g. $TiCl_3$ x-$AlCl_3$, the most commonly used value being $x=0.3$. Supported catalysts are also heterogeneous, and depending upon the dispersion of the transition metal atom, the efficiency of the catalyst increases. Some examples of commercial Ziegler-Natta catalysts which are heterogeneous are given in Table 3.

Table 3 — Commercial Heterogeneous Catalysts

No.	Trade name	Commercial firm	Presumed catalyst composition
1	Stauffer A	Stauffer Chemical Co., USA	$TiCl_3$
2	Stauffer AA	Stauffer Chemical Co., USA	$TiCl_3.0.3\ AlCl_3$
3	Toho 140 Series	Toho Titanium Co., Japan	$TiCl_3.0.3\ AlCl_3$
4	Solvay	Solvay et Cie, Belgium	$TiCl_3.0.3\ AlCl_3$ diisoamylether
5	Toho 144	Toho Titanium Co., Japan	$TiCl_3.0.3\ AlCl_3$ electron donor
6	Lynx-900	Catalyst Resources Inc.	Unsupported titanium chloride modified
7	FT/KT Series	Himont Inc., USA Mitsui Petrochemicals Co., Japan	Supported catalyst

Table 4 — Homogeneous Ziegler-Natta Catalysts

No.	Catalyst	Olefin	Structure
1	$TiCl_4$ + Et_2AlCl	Ethylene	Linear PE
2	Cp_2TiCl_2+Et_2AlCl	Ethylene	Linear PE
3	VCl_4+Et_2AlCl below −45°C	Propylene	Syndiotactic PP
4	VCl_4+Et_2AlCl	Ethylene and propylene	Random copolymer
5	Cobalt octoate+ Et_2AlCl	Butadiene	*cis*-1,4-polybutadiene
6	$TiCl_4$+Et_3Al	Isoprene	*cis*-1,4-polyisoprene

The soluble or homogeneous catalysts have achieved importance both for manufacture of specific polymer and for mechanistic studies. Catalysts derived from dicyclopentadienyl titanium dichloride and triethylaluminium or diethylaluminium chloride were first discovered by Natta and coworkers as soluble catalysts for the polymerization of ethylene[21]. A homogeneous catalyst composition consisting of vanadium tetrachloride and diethylaluminium chloride at −78°C produces exclusively syndiotactic polypropylene[22]. Certain soluble catalysts in which sites are all nearly identical produce copolymers that have a random or moderately alternating distribution of comonomer units[23]. Combinations of vanadyl esters or vanadyloxy chloride with aluminium chloroalkyl are best examples in this class. Representative examples of homogeneous catalyst are given in Table 4.

In addition to these two, some authors also refer to 'colloidal catalysts'. When certain aluminium alkyls are combined with transition metal salts bearing alcoholate, acetylacetonate or organic ligands, the resulting catalysts are sometimes described as 'soluble' or 'apparently soluble'[24].

The efficiency of a catalyst is often dependent on its physical state. According to accepted thesis, homogeneous catalysts would always be more efficient than heterogeneous, since every available transition metal (active centre) is considered to be of equal reactivity in the former. In the heterogeneous Ziegler-Natta catalyst only a small fraction of the transition metal atoms are active at any time, typically about one mole per cent or less. In effect, the remaining transition metal salt acts as a bulk support for the few active centres. The physical state of the catalyst also decides polymer properties like morphology, copolymer composition and microstructure. Since catalyst particles are templates for polymer growth, a hetergeneous catalyst with a controlled particle size can be used to produce polymer particles also of controlled particle size. Till recently it was generally accepted that heterogeneous catalysts promoted isotactic polymerization of propylene whereas homogeneous catalysts produced atactic or syndiotactic polypropylene. Recent developments in soluble catalysts (see section 3) have proved this to be no longer true.

2.2 Kinetic features of Ziegler-Natta catalysts

The kinetics of Ziegler-Natta polymerization provides important information regarding the process. This kinetic interest arises because of a deliberate interplay between a number of operational factors such as catalyst physical state, choice, absolute concentration, etc. Kinetic data also provide information on the rate law, activation energy, number of active centres, average lifetime of the growing polymer chain, etc., which are of importance in the formulation of models or mechanisms for the reactions. From a practical point of view, the kinetic data also provide sufficient basic information for process engineering.

The basic kinetic aspects of Ziegler-Natta catalysis and polymerization have been well discussed by Keii[25] and Zakharov *et al.*[26]. While interpreting kinetics of heterogeneous catalysts it is necessary to consider the following rather complex situations: (1) the creation of active centre on metal surfaces, (2) the diffusion of monomer from gas to the liquid phase and to the active centre, and (3) the polymerization leading to the formation of a semicrystalline phase in the pores of the catalyst thus disintegrating the catalyst particles and exposing new surfaces and allowing new centres to form. An apparently simpler situation should exist for a homogeneous catalyst, since the active centre is part of a single molecular metal complex and distributed equally within the reaction. But since all soluble catalysts give a decay type rate curve, the above conclusion is deceptive because here a bimolecular interaction between active centres is possible, leading to termination of the active centre. Also, a true homogeneous catalyst is non-existent in any polymerization system because the polymer precipitates out of solution within a short time from the commencement of reaction and thereon assumes all the characteristics of the heterogeneous system.

There are many factors that can influence the kinetic results. The factors can either be related to the catalyst such as choice, stability, etc. or related to polymerization condition such as concentration of monomer, mass transfer, time, temperature of polymerization, etc. Natta and Pasquon[27] demonstrated that particle size of the catalyst has immense effect on the kinetics. Comparison of ground and unground titanium trichloride shows that ground titanium trichloride reduces the initial build up period and attains maximum rate very quickly. Since titanium trichloride and diethylaluminium chloride is a heterogeneous system, this change has been attributed to the easy capture of smaller titanium trichloride particles in ground catalyst compared to unground ones.

The kinetic aspects of high activity supported Ziegler-Natta catalysts have been widely studied[28,29]. It is interesting to note that the kinetic features are entirely different for ethylene and propylene. A high activity catalyst proposed for ethylene shows little activity for propylene[30]. In general, the rate of polymerization of ethylene is much higher than that of propylene. Also in case of ethylene most high activity catalysts show a "build up" type of kinetic curve, that is, rate increasing and reaching a constant value after about 30 min. High activity catalysts for propylene on the other hand show a rapid decay of rate after reaching very high initial rates.

Therefore, the kinetic behaviour of non-stationary polymerization should be examined by means of a suitable kinetic method[31]. The fact that the polymerization activity with supported catalysts decays with time has been the subject of various studies[32-36]. Two main possible reasons were discussed, namely the diffusion factor and the chemical change in the catalyst structure during the course of polymerization. The polymer is formed in the pores of the heterogeneous catalyst and as the polymer becomes larger there may be a diffusional hindering of the different components to the catalyst site. This leads to a temperature gradient within the particle and the medium surrounding it resulting in decrease in activity. The argument in favour of chemical change concerns the nature of donor-aluminium alkyl interactions, which are very fast and known to degrade in a short time[37,38]. The effect of mass transfer is also significant in the case of high yield catalysts just as in the conventional catalyst[31].

2.3 Nature of active centres and their determination

The kinetics and mechanism of Ziegler-Natta catalysts can be better understood in terms of the nature and number of active centres. It has been generally accepted that polymer growth occurs on an active site located on the surface of the titanium trichloride catalyst. Literature evidence now favours the occurrence of this active centre due to the alkylation of titanium trichloride by the metal alkyl (Fig. 3). The active centre is now considered as a titanium centre with both an alkyl substituted and a chlorine vacancy located on the edge of the titanium trichloride crystals. The growth occurs by two steps: (1) the complexation of the monomers on the active site, and (2) further insertion of monomer between transition metal-carbon bond.

Two kinetic models and theories have been reported in the literature to explain the origin and significance of these active centres. Since the metal alkyl is responsible for creating active centre, according to the Langmuir -Hinshelwood model[39], the polymerization rate should increase with increasing concentration of metal alkyl. According to the Riedel model[40], the monomer comes directly from solvent or gas, hence the rate is independent of metal alkyl.

Perhaps the greatest evidence for active centre comes from metal alkyl-free catalysts where one does not use an alkylaluminium compound as an activator. In case of titanium trichloride, it has been found that the active sites could be located on the basal plane, edge or corner of Ti crystal lattice. Microscopic examination of polymer growth suggests that the sites located on the basal planes are comparatively inert being buried in a layer of chloride ion matrix[41]. The solid state structure of the catalysts have also been related to the polymer stereoregularity[42-45].

Various methods are employed for the determination of active centres in catalytic polymerization of olefins[46,47]. The following are the most important: (i) determination of the number average molecular weight from gel permeation chromatography and finding the number of polymer chains produced per titanium atom; (ii) using radiotracer technique and introducing radioactivity into the growing polymer chain (The use of radioactive alcohols is the classical example of this technique); and (iii) quenching with labelled carbon monoxide and carbon dioxide. The use of radioactive alcohols give ambiguities due to the reaction of alcohol with aluminium-polymer bond. More widely employed are the selective tracer such as carbon monoxide and carbon dioxide which interacts only with titanium-polymer bond. However this method is also the subject of criticism because of the reversible character of the quenching reaction and other side reactions involved[46]. There are also some indirect methods available, such as adsorption of allene[48] and quenching with sulphur dioxide and measuring the amount of sulphur on polymer[49] but these are not widely employed. It follows that none of the quenching methods have universal applications, and the literature data should be compared with caution.

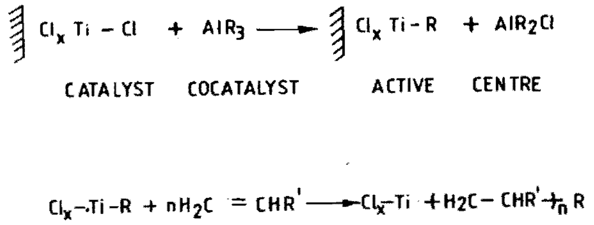


Fig. 3—Formation of active centre on titanium catalyst.

The number of active centres (C^*) depends on the method of preparation of the catalyst and its composition. Table 5 gives some of the values for active centres in both conventional and supported catalyst systems. For $TiCl_3$, AA type, the number of propagation centres are considerably higher than in titanium dichloride system, and reaches 0.8×10^2 mol/mol of Ti. With supported catalyst a very dramatic increase in C^* is achieved with very rapid formation of active centres compared to conventional titanium trichloride and a high increase in the propagation rate constant. The reasons behind high activity of such catalysts have been explored by measuring the concentration of active sites as well as determining the kinetic rate, and conflicting views have been expressed[31]. It has been suggested that in the case of ethylene the increase in activity is a result of increase in active site concentration whereas for propylene it is due to increase in rate of propagation[50-52].

2.4 Factors determining catalyst activity

The mode of action of the Ziegler-Natta catalysts has been the subject of intense investigations over the past three decades. It follows from these studies that the efficiency of the active catalyst centre is influenced by (a) the nature, valency state, and type of ligands attached to the transition metal, (b) the type of organometallic cocatalyst, (c) physical morphology of the catalyst, (d) added internal and external electron donors, and (e) conditions of polymerization. The ability to manipulate effectively these parameters has

Table 5—Number of Active Centres (C^*) and Propagation Rate Constant K_p in Ziegler-Natta Catalyst

No.	Monomer	Catalyst	Cocatalyst	Method	$C^* \times 10^2$ mol/mol.of Ti	$K_p \times 10^2$ L.m^{-1}s^{-2}	Ref.
1	Ethylene	$TiCl_3$.AA	Et_3Al	^{14}CO	0.03	100	50
2	Ethylene	$TiCl_4/MgCl_2$	Et_3Al	BuOT	770	140	49
3	Ethylene	$MgCl_2/TiCl_4$	Et_3Al	^{14}CO	300	130	26
4	Ethylene	$RMgCl/TiCl_4$	Et_3Al	^{14}CO			49
5	Propylene	$TiCl_3$.AA	Et_3Al	^{14}CO	0.8	3	31
6	Propylene	$TiCl_3$.AA	Et_2AlCl	^{14}CO	0.5	3	31
7	Propylene	$TiCl_3$. electron donor	Et_2AlCl	^{14}CO	0.9	10	29
8	Propylene	$MgCl_2/TiCl_4$/EB	Et_3Al	^{14}CO	1.6	15	31
9	Propylene	$MgCl_2/TiCl_4$/EB	Et_3Al	^{14}CO	1.2	16	50
10	Propylene	$MgCl_2/TiCl_4$	Et_3Al	$\bar{M}n$	20	24	51,52
11	Propylene	$MgCl_2$/EB/$TiCl_4$	Et_3Al/EB	$\bar{M}n$	2.8	270	51
12	Propylene	$TiCl_3$.AA	Et_3Al	Allene adsorption	1.4	13	48

EB=ethyl benzoate

led to the development of improved catalysts for olefin polymerizations.

2.4.1 *Transition metal*

The nature of transition metal, its valency state and the ligand environment around the metal influence the efficiency of metal centre towards polymerization. Recent studies by Soga and coworkers[53] have shown that in supported titanium catalysts whereas Ti^{3+} is active for both ethylene and propylene polymerization, Ti^{4+} and Ti^{2+} are only active for ethylene polymerization. Kashiwa and Yoshitake[54] showed that a ball milled $MgCl_2$-$TiCl_4$ catalyst in which titanium is in a 4 + valence state showed polymerization activity for both ethylene and propylene, whereas the same catalyst when prereduced with Et_3Al to 80% Ti^{2+} and 20% Ti^{3+} showed a diminished activity for ethylene polymerization and no activity for propylene polymerization. However, in all these cases, the valence state of titanium refers to the initial state and not the actual state participating in polymerization as the catalyst underwent further reduction in the presence of added Et_3Al and propylene during polymerization. Chien and Wu[55] and Zakharov *et al.*[56] have studied the states of titanium ion in titanium-magnesium catalysts. Using EPR it was shown that only about 20% of Ti^{3+} were observable, the remaining 80% being EPR silent. Chien and Wu interpreted this observation in terms of two types of Ti^{3+} centres, attached to $MgCl_2$ surface, one which is coordinatively unsaturated and the other chlorine bridged to an adjacent Ti^{3+} species. Further reduction of this catalyst with free Et_3Al or Et_3Al methyl-*p*-toluate complexes produced more EPR active Ti^{3+} species. Zakharov *et al.* reported EPR results with a ball milled $TiCl_3$. 0.3 $AlCl_3$-$MgCl_2$ catalyst. Milling caused a drastic increase in the content of Ti^{3+} ions observed in EPR. This was attributed to better dispersion of $TiCl_3$ on support resulting in the formation of isolated Ti^{3+} ions. Additional EPR active Ti^{3+} ions, not observed in the original $TiCl_3$, were also found after milling. As observed earlier by Chien and Wu, it was found that approximately 80% of Ti^{3+} were EPR silent and were attributed to $TiCl_3$ surface aggregates. The increase in polymerization activity of catalyst with decreasing titanium content was ascribed to increasing dispersion of $TiCl_3$ on $MgCl_2$. Using $TiCl_4$-$MgCl_2$ catalyst, the effect of prereduction with organoaluminium compound, prior to its use in polymerization was studied by EPR. It was found that mild prereduction with Et_3Al did not significantly affect activity. However reduction with Et_3Al at higher Al/Ti ratio or higher temperature or reduction with Et_2AlCl led to reduced activity and decreased EPR intensity of Ti^{3+} ions. This was attributed to formation of surface aggregates and not to reduction of Ti^{3+} to Ti^{2+}.

These results appear to indicate that Ti^{3+} which is coordinatively unsaturated and not located in a purely chlorine environment are responsible for polymerization activity. However, there is little understanding of the structure of several EPR active Ti^{3+} species formed during Et_3Al reduction of such catalysts. Although EPR inactive Ti^{3+} species are believed to be finely dispersed particles or surface aggregates of $TiCl_3$, they can become active centres for polymerization by interacting with organoaluminium compounds. Suffice to conclude that titanium oxidation states on supported catalysts are not monolithic and our understanding of the effect of oxidation states on polymerization activity is far from complete. Further insights can be obtained only when techniques are designed to observe metal oxidation states during actual polymerization.

Although ligands around titanium are believed to exert considerable influence on catalyst activity, little has been reported in published literature. Using a ball milled $MgCl_2$-TiX_4 ($X=N(C_2H_5)_2$, OPh,Cl) catalyst, Zucchini and coworkers[57] polymerized ethylene in presence of tri-isobutylaluminium. It was found that catalyst activity increased in the order $N(C_2H_5)_2 < OBu < OPh < Cl$. This is the reverse order to the ligand electron-releasing ability. Similarly studies with a series of $TiCl_n(OBu)_{4-n}$, where $n=0$–4 showed that polymer yield increases with the value of n. Bulky alkyl groups in $Ti(OR)_4$ reduced polymerization activity. Tetra (2,4,6-trichlorophenoxy) titanium gave a lower polymer yield than tetraphenoxy titanium. It was hypothesised that increase in positive charge on titanium atom caused an increase in catalyst activity.

In unsupported titanium halide/alkylaluminium systems, it has been found that polymers of high isotactic regularity are obtained when the halogen is an iodide ligand. In an elegant study of the stereochemistry of the first propylene insertion step by ^{13}C-NMR, Locatelli and coworkers[58,59] found that presence of alkyl ligand greater than methyl and a halide ligand greater than chlorine enhances the enantioselectivity of the insertion of the first monomeric unit.

2.4.2 *Alkylaluminium compound*

Metal alkyls containing group I-III metals form active metal alkyl cocatalysts in olefin polymerization, the most commonly used being aluminium alkyls. With titanium trichloride it was found that rate of propylene polymerization was in the order of triethylaluminium >diethylaluminium chloride>ethylaluminium dichloride. However, stereospecificity was highest with diethylaluminium chloride, thus making it the preferred catalyst. With diethylaluminium chloride it has been found that relative weight ratio of Cl/Al, has a significant effect on catalyst activity and isotacticity, the optimum being 1.32[60]. In the case of highly active supported catalysts it has been generally found[61-63] that diethylaluminium chloride produces catalyst of lower activity and polymer of lower isotacticity than trialkylaluminium. The reasons for this are not clearly understood. It is speculated that during polymerization, first reaction of monomer is the association with alkylaluminium compound. Such association is more favoured with Et_3Al (which is present in monomeric form in hydrocarbon to the extent of 15-18%) than with dimeric Et_2AlCl, thus accounting for the higher efficiency of Et_3Al as cocatalyst[64]. The explanation appears rather tenuous. Although the authors found that with Et_2AlCl, the extent of reduction of Ti^{4+} to Ti^{3+} was only 29.3% against 41.5% for Et_3Al, this was not considered sufficiently important to explain the lower efficiency of Et_2AlCl. In a recent study it has been found that the efficiency of Et_2AlCl can be substantially enhanced by addition of alkylmagnesium or alkyllithium and such catalysts were even superior to trialkylaluminium[65]. The best results were obtained when $Et_2AlCl/MgBu_2$ ratio was 2. The possibility of *in-situ* generation of trialkylaluminium under these conditions appears unlikely. Surprisingly, magnesium alkyls deactivated the trialkylaluminium cocatalyst. The nature of aluminium alkyl also determines the type of kinetics one observes with propylene polymerization. Unlike trialkylaluminium, tri-isoprenylaluminium is reported to give a "build-up" type kinetic curve, the rate increase reaching a constant value after about thirty minutes[66].

Possibility of replacing alkylaluminium cocatalysts in Ziegler polymerization by titanium alkyls has recently been reported[67]. Used along with a Mg-Ti catalyst, the efficiency of $(MeCp)_2TiMe_2$ cocatalyst is lower by a factor of ten compared to trialkylaluminium. Interestingly, the value of isotactic index was very high (~96%). Such high values of isotactic index can be achieved with Et_3Al only by addition of an electron donor.

2.4.3. *Physical state of the catalyst*

The physical morphology of the transition metal catalyst has the most dramatic effect on both polymerization activity and polymer properties. The occurrence of various crystalline modifications of titanium trichloride, their method of synthesis and their effect on polymerization activity was one of the seminal discoveries in this field and led to the synthesis of isotactic polypropylene[3]. It was later shown that the lattice defects in titanium trichloride are responsible for polymer growth[68]. Simple grinding of titanium trichloride led to higher polymerization activity presumably due to an increase in lattice disorder[69]. The crystallite size and crystallite surface area have also been alluded to as important factors in determining activity of a transition metal catalyst[70]. A linear relationship between polymerization rate and crystallite surface area (not BET surface area) has been observed. In view of the extensive disintegration of the catalyst, the working surface area of a $TiCl_3.0.3\,AlCl_3$ catalyst has been estimated to be about 70-80 m^2/g. These catalysts also lead to polymer particles with a broad particle size distribution as the polymer replicates on the catalyst with a fairly predictable relationship between the particle shape as well as size distribution of the catalyst and polymer. However, because of disintegration of catalyst during polymerization, the particle size distribution of polymer bears little resemblance to that of the original catalyst.

One of the forerunners of today's generation of high yield and high isotacticity catalysts was the "Solvay" catalyst developed by Solvay et Cie, Belgium. The catalyst which is predominantly δ-titanium trichloride is prepared by a multistep process consisting of initial complexation of titanium tetrachloride with diisoamyl ether, reducing it with diethylaluminium chloride and grinding the mixture[71]. It is believed that the reason for higher activity is the high specific surface area due to selective extraction of aluminium compounds contained in the crystalline titanium trichloride derived from reduction of titanium tetrachloride with diethylaluminium chloride. Further improvement in the catalyst has been made by use of alternative extracting agents and introduction of a grinding step in the catalyst preparation procedure[72-75].

The high activity Ziegler-Natta catalysts invariably use an inorganic support as a high surface area carrier. A perusal of the vast patent literature suggests that anhydrous activated magnesium chloride is the support of choice. This is presumably due to the crystalline similarity of magnesium chloride (ionic radii of Ti^{4+} or Ti^{3+} =0.68 Å, Mg^{2+}=0.65 Å) and titanium trichloride and the ability of the support to maximize the reactive sites by packing Ti at the edge of the carrier. X-ray evidence indicates that Ti^{3+} or Ti^{4+} can be effectively dispersed on magnesium chloride lattice forming 'surface' mixed crystals[28]. The catalyst support influences both polymerization rate and tacticity of the polymer. A relationship has been observed between the tacticities of polypropylene produced and the ionic radius of the metal of the support[76].

The method of preparation of anhydrous magnesium chloride as well as its activation has a significant effect on the activity of the final catalyst. Anhydrous magnesium chloride can be activated by prolonged milling which results in an increase in surface area[77]. However, it has been found that grinding for more than 20h led to loss of activity[78]. It was presumed that initial increase in activity with grinding was due to decrease in crystalline order, increase in energetically specific sites and surface area. Prolonged grinding was believed to cause site agglomeration. Treatment of mangesium chloride with ethyl benzoate (EB) resulted in formation of a new crystalline phase which could be milled for as long as hundred hours without any adverse effect on catalyst activity. A strong complex formation between magnesium chloride and ethyl benzoate was suggested[79,80]. The crystalline particle size of magnesium chloride decreases with increasing ethyl benzoate, reaches a minimum at $EB/MgCl_2$=0.17 beyond which it increases, even above the original level observed for pure magnesium chloride. A molar ratio of ethyl benzoate to magnesium chloride of 0.17 represents the support of most favourable polymerization properties. A detailed structural investigation of magnesium chloride activated by milling with titanium tetrachloride has been reported[81,82,52]. It was observed that surface area was nearly constant up to 40h of milling while the crystallite dimensions continuously decrease with milling, probably due to crystallite reaggregation. The activity of catalyst for ethylene polymerization also increased up to 70h of milling beyond which the activity decayed. No satisfactory correlation could be obtained between crystallite size, surface area and catalyst activity.

It has been found that dramatic changes in the surface property of magnesium chloride can be brought about by chemical processes of activation thus avoiding the physical milling process. The chemical processes cited in patents[83-85] include treatment with alcohols such as ethanol or 2-ethylhexanol and other *in situ* methods of generation of magnesium chloride. The nature of compositional and structural changes occurring in the support during various stages of catalyst preparation using chemical activation techniques has been reported recently[86].

The use of inorganic supports in addition to conferring the properties of high specific surface and porosity also make the catalyst less prone to disintegration due to thermal/mechanical stress. Thus it is possible to take advantage of the replication phenomena and generate polymers in desired shape and particle size of the support. Methods to preform magnesium chloride in specific shape and size have been reported[87]. Under conditions in which no disintegration occurs during polymerization, polymer particle size is directly proportional to the total polymerization rate and is given by the equation[28].

$$R_\mathrm{t} = \sqrt[3]{\frac{3}{4\pi\delta N}\int_0^t R_\mathrm{p}\,\mathrm{d}t}$$

where R_t=radius of growing polymer at time t; R_p= total polymerization rate ($gL^{-1}\ h^{-1}$); δ=density of polymer (g/cm³) at polymerization conditions; and N =number of polymer granules per litre of reagent phase.

Recent patents[88-90] also allude to a prepolymerization step under mild and controlled conditions (25-40°C, 1-4 kg/cm² propylene pressure) with some of the high activity catalysts. This presumably minimizes the thermal effects on catalysts when monomer is contacted with catalysts leading to better catalyst performance and particle size control.

The physical characteristics of Ziegler-Natta catalysts are summarized in Table 6.

2.4.4 Role of internal and external donors

The use of Lewis bases in Ziegler-Natta catalysts dates back to the sixties when improvements in stereospecificities of conventional $TiCl_3$-based catalysts were reported[19]. However, not until the advent of the high activity polymerization catalysts did electron donors become an integral part of the catalyst systems.

Table 6—Physical Characteristics of Ziegler-Natta Catalysts

No.	Catalyst	Preparation Method	Surface area m^2/g	Bulk density g/cc	Pore volume mL/g	Polym. activity kg/g Ti	Ref.
1	$TiCl_3.0.3\ AlCl_3$	Reduction of $TiCl_4$ with Et_2AlCl	40-50	0.1	0.2-0.3	1 (PP)	19
2	$TiCl_3$.diisoamyl ether	Reduction of $TiCl_4$ diisoamylether complex with Et_2AlCl	140-200	0.1-0.2	0.1-0.2	1-10 (PP)	29
3	Supported Ti	Milling $TiCl_4$ with a mixture of $Mg(OH)_2$ and $MgCl_2$	60	0.23	0.312	250 (PE)	30
4	Supported Ti	Milling $TiCl_4$ with $MgCl_2$	200	0.4-0.5	1-2	200 (PP)	7
5	Supported Ti	Milling $MgCl_2$ for 70 h at 35 °C with $TiCl_4$	98	0.5	0.8-0.9	290 (PE)	81
6	Supported Ti	Liquid phase treatment of $MgCl_2$. EtOH complex with Et_3Al,EB and $TiCl_4$	300-500	0.4-0.5	1-2	220 (PP)	83

In the current generation of high activity-high stereospecificity polyolefin catalysts, electron donors are used in the preparation of solid titanium catalysts (internal electron donor) and also along with alkylaluminium compound (external electron donors). A great deal of research has since been conducted in an attempt to delineate the role of both internal and external donors on catalyst activities and stereospecificities. Although a complete understanding is still lacking, it is well recognized that the judicious choice of electron donors may well hold the key to the tailoring of polyolefin catalysts.

One of the most effective ways of preparing a Ti-Mg catalyst involves (i) milling of an electron donor, usually ethyl benzoate (EB) with anhydrous magnesium chloride; and (ii) treatment of the product with titanium trichloride. A number of studies have attempted to clarify the role of EB in such catalyst preparations[78–80,91,92]. The following are the salient conclusions : (a) Milling of $MgCl_2$ and EB causes a decrease of the size of $MgCl_2$ crystallites, the minimum size being attained at a EB/$MgCl_2$ mole ratio of 0.17; (b) Introduction of EB into $MgCl_2$ also causes a reduction in surface area; (c) A monolayer distribution of the molecular complex $MgCl_2$-EB over the surface of $MgCl_2$ crystallite is indicated under these conditions; (d) Combination of small crystallite dimensions and small surface area is indicative of the presence of an agglomerate of $MgCl_2$ crystallites held together by complexation with EB; (e) Treatment of $MgCl_2$ -EB with $TiCl_4$ results in removal of part of EB as $TiCl_4$ -EB complex and inclusion of $TiCl_4$ into $MgCl_2$ layers; (f) This results in a sharp increase in surface area and an increase in $MgCl_2$ crystallite size in the (110) direction, suggesting that $TiCl_4$ complexation occurs on the side face of the crystallites, where coordinatively unsaturated magnesium atoms are located. Thus the major role of EB appears to be its ability to efficiently fix $TiCl_4$ on $MgCl_2$ surfaces[93].

A large number of external electron donors are used in conjuction with organoaluminium compounds to improve the stereospecificity of high activity catalyst in propylene polymerization. Most common are esters of aromatic acids and alkoxysilanes. A number of studies report on the reaction of alkylaluminium with esters[37,94–97]. It is generally agreed that such reactions lead to the formation of aluminium alkoxides (both primary and *t*-alkoxy derivatives of aluminium) which in conjuction with trialkylaluminiums are responsible for enhanced stereospecificities. Sivak and Kissin[98] have found that interaction of Et_3Al with several tertiary alcohol with branched aryl or alkyl groups showed a modifying effect approaching that for aromatic acid esters. The implication was that the resulting alkoxyaluminiums were similar to the product of reaction of aluminium alkyl with aromatic esters. In a related study Yano and coworkers[99] found that the reaction of Et_3Al with methyl-*p*-toluate is suppressed in presence of propylene and no reduction products are obtained. Use of preformed hemialkoxides by reaction of Et_3Al with *t*-phenylcarbinols was less effective. Isotacticities could be reasonably well correlated with Hammet's σ or carbonyl wave numbers (IR) for a series of *p*-substituted ethyl benzoates. Kashiwa has studied the mechanism by which external donor affects the stereospecificity and productivity of a polypropylene catalyst[52,100,101]. It was concluded that (a) at least some part of the EB added to the polymerization system acts upon the solid catalyst and is fixed on to the solid catalyst, (b) EB selectively poisons the active sites responsible for atactic polymer, (c) ester increases the K_p value of isotactic sites, and (d) there appear to be two sorts of isotactic sites, one associated with the ester and the other free. The sites associated with esters lead to formation of high molecular weight isotactic polymer. A detailed kinetic study of a ball milled $MgCl_2$-$TiCl_4$ catalyst by Keii and coworkers led to the conclusion that complexation of EB with Et_3Al, reducing its effective concentration and the selective poisoning of the atactic acid sites were responsible for the enhancement effect of EB on the stereospecificity of the catalyst[102]. Soga and coworkers[103] have described the active site on a Mg-Ti catalyst as a Ti^{3+} centre, one having two Cl vacancies (atactic) and the other having only one Cl vacancy (isotactic). EB complexes preferentially with the former sites. Pino and coworkers[104] suggest that two types of stereospecific catalytic centres exist, in one of which the EB is present. The centres can be classified according to their Lewis acidity, the more acidic centres yielding polymers with lower molecular weight and tacticity. The added EB distributes itself between the catalytic centres in the solid phase and the trialkylaluminium in solution. The combined role of internal and external bases (ethyl benzoate) has been studied[105,106]. It was found that decrease in polymerization rate by external donor was more severe in the absence of internal donor; also in the absence of internal donor, external donor is unable to increase the isotacticity index (I.I) beyond 88%. Similarly, in the absence of external donor, aluminium alkyl removes 90% of internal donor from $MgCl_2$ surface. This also results in lower stereospecificity. Thus the roles played by EB as internal and external donor are complementary. Barbe and coworkers[107] have investigated the role of three external donors, namely, methyl-*p*-toluate (MPT), 2,2,6,6-tetramethylpiperidine (TMP) and phenyltriethoxysilane (PES) with a Ti-Mg catalyst prepared by chemical activation method and containing no internal donor. Hindered bases have been previously reported to be very effective in enhancing isotacticity without reducing catalyst activity[108]. However, the present study showed that with MPT and PES, at low donor concentrations, an increase in producitivity was observed, whereas for TMP, isotacticity increased at low donor concentrations, but with MPT such an increase was observed only at higher concentrations. Such a trend was also observed with polymerization rates with MPT and PES. Thus it was concluded that at low concentrations, the donors stabilize the active centres whereas at higher concentrations they poison the active centres.

In conclusion, the role of donors in high efficiency propylene polymerization catalysts defies a simple explanation. Depending on the catalyst, the reaction conditions and the nature of donor, one or more of the following phenomena may assume importance : (a) selective poisoning of non-stereospecific sites, (b) increase in number and/or the rate of propagation of active sites, (c) complexing and removal by donors of inhibitors of active sites, (d) reduction in reducing power of aluminium alkyls, and (e) stabilization of active centre structure and chirality by electron donor.

2.4.5 Reaction parameters

Catalyst activity of Ziegler-Natta catalysts also depends upon the process conditions under which polymerization is conducted. Conventionally, these include residence time, temperature, reaction pressure, ratios of Al/Ti, nature of donor and its concentration and the nature of diluent. Compared to conventional catalysts which use an Al/Ti weight ratio of 3, high activity catalysts employ very high Al/Ti ratios, ranging anywhere between 50 and 200. With a high activity catalyst prepared from magnesium chloride, ethyl benzoate and titanium tetrachloride maximum polymer productivity was observed[31,109] when the titanium content was around 2.5%. Both higher and lower titanium content led to loss of productivity. Such an observation has been found to be general in high activity catalysts. In general, catalyst activity shows a steady increase with temperature up to 85°C beyond which thermal activation of catalysts leads to loss in activity. In case of propylene and with high activity catalysts isotacticity index increases with temperature which is very unlike the behaviour of conventional titanium trichloride[110]. Whereas catalyst activity increases with residence time, isotacticity index shows a rapid decrease with residence time. This has been attributed to the decrease in ratio between isotactic and atactic specific sites caused by chemical reactions between the catalyst and the electron donor which is added to the catalyst to enhance stereospecificity[37,38]. The polymerization rate as well as its productivity predictably increase with the partial pressure of monomer in the polymerization system. With monomer as a diluent (liquid propylene), gas-liquid mass transfer effects on polymerizations disappear leading to 50% increase in catalyst activity (Table 7). Hydrogen, which is employed as a chain transfer agent, is believed to exert an activating influence on propylene polymerization using high activity catalysts and deactivating effects on ethylene polymerization using the same catalyst[111]. The reason for this is not clear at the moment. Hydrogen is also believed to exert a deleterious effect on polymer isotacticity[112]. The role of hydrogen on Ziegler-Natta catalysts has been recently reviewed[113].

2.5 Effect of catalysts on polymer properties

The most important properties that are critical to

Table 7—Relative Performance of Ziegler-Natta Catalysts in Hydrocarbon Slurry and Liquid Pool Process

Catalyst	Cocatalyst	Process[a]	Catalyst activity kg/g cat.	I.I%
$TiCl_3.0.3\ AlCl_3$	Et_3Al	Heptane slurry	0.65	90
$TiCl_3.0.3\ AlCl_3$	Et_3Al	Liquid propylene	1.6	90
Supported $TiCl_4$.on $MgCl_2$	Et_3Al	Heptane slurry	5.5-7	91-93
Supported $TiCl_4$.on $MgCl_2$	Et_3Al	Liquid propylene	9.0-11	92-94

[a] Reaction condition (i) for heptane slurry process : 70° C, 2 h and 10 kg/cm^2; (ii) for liquid propylene process : 70° C, 2 h and 30 kg/cm^2; Ref. 110

the applications of polyolefins and which are at least in part determined by the catalysts are (1) molecular weight, (2) molecular weight distribution, and (3) crystallinity or stereoregularity.

2.5.1 Molecular weight

The basic composition of catalyst and its characteristic operating conditions determine the range of molecular weight obtainable. Some catalysts (CrO_3-SiO_2) exhibit a sharp dependence of molecular weight on polymerization temperature and hence temperature can be used to regulate molecular weight. Polymer molecular weights produced by Ziegler-Natta catalysts are, however, less sensitive to temperature. Consequently control of molecular weights is invariably achieved by addition of a chain transfer agent, the most common being hydrogen and diethylzinc. In general, molecular weight shows an inverse relationship to the square root of hydrogen partial pressure. More precise relationships for specific catalyst systems have been derived[113].

2.5.2 Molecular weight distribution (MWD)

Control of molecular weight distribution by manipulation of catalyst compositions is increasingly becoming important. A comprehensive survey of patent and published literature on this topic has recently appeared[114]. The breadth of molecular weight distribution generally observed with heterogeneous Ziegler-Natta catalysts has been interpreted based on a diffusion theory and a chemical theory. The former suggests that hindrance to monomer diffusion towards the surface of the catalyst granule caused by its progressive encapsulation by the polymer is responsible for broad MWDs. The latter attributes this observation to plurality of active centres on catalysts with differing reactivity.The latter hypothesis appears more reasonable in view of the fact that perfectly soluble catalysts containing homogeneous active centres are capable of producing narrow MWD polymers even under conditions where the polymer precipitates (slurry polymerization) and broad MWD can be obtained even when operating under conditions wherein the polymer and catalyst are both dissolved in reaction diluent.

Considerable literature exists to demonstrate that with homogeneous catalytic systems, polymers with narrow MWD can be prepared under controlled conditions. However, polymers with broad MWD and even with bi-or trimodal curves result from physical or chemical transformations undergone by the catalyst system just prior to or during polymerization.

Apart from the physical state of the catalyst, MWD variation can be brought about by changes in the transition metal, the ligands and oxidation state of the transition metal and the alkyl aluminium cocatalyst. Multiple metals in catalysts (Ti + V, Ti+Zr, Ti + Ni) can cause broadening of MWD, presumably by creating active centres of differing reactivities. Using titanium halide based magnesium chloride supported catalysts it was found that breadth of polyethylene MWD increased with an increase in electron acceptor power of the halide ligand. It has also been demonstrated that degree of reduction of Ti^{4+} can be used to control MWD as the polymer formed by Ti^{3+} active centres has a much lower index of polydispersity than that formed by Ti^{4+} sites. Number of studies have pointed out the dependence of MWD on the nature of ligand associated with aluminium. For propylene and ethylene polymerization delta-$TiCl_3$ and $V(acac)_3$ catalyst, respectively, the polymer polydispersity decreases in the order :

$Al(C_2H_5)_2Br > Al(C_2H_5)_2\ Cl > Al(C_2H_5)_3$

Additives such as water which react with alkylaluminium also alter MWD. Although the MWD of propylene was found to be independent of Al/Ti ratio ($TiCl_3$-$AlEt_2Cl$), the MWD of polyethylene was affected by Al/Ti ratios [$(C_5H_5)_2\ TiCl_2$-$AlEt_2Cl$].

Most catalysts for propylene polymerizations consist of an externally added electron donor or polar adjunct which alter the nature of catalysts by complexing with the individual components and enhance the stereoregulating ability of the catalyst *(vide supra)*. The third component could therefore be used as a potential tool for MWD regulation although literature provides few examples where this has been achieved. It has been found that MWD curve of the boiling heptane insoluble (isotactic) fraction of polypropylene prepared using magnesium chloride-titanium tetrachloride and triethylaluminium-ethyl benzoate catalytic system shows two peaks[100]. The position of the lowest molecular weight peak corresponds to the polymer obtained in the absence of ethyl benzoate, while the highest molecular weight peak increases with the increase of donor/Al ratio causing MWD to broaden. This led the author to conclude that at least two types of isotactic active centre exist, of which the one producing the polymer with higher molecular weight is ester associated. Electron donors such as aromatic esters are known to increase polymer molecular weights when incorporated in catalyst systems[19]. Barbe and coworkers[107] have found that increasing donor/Ti ratio causes broadening of MWD. Further, they found that at donor/Ti=5-7, methyl *p*-toluate gave a bimodal MWD whereas 2,2,6,6-tetramethylpiperidine and phenyltriethoxysilane gave monomodal MWD.

The use of supports in the high activity polymerization has introduced another variable which can affect polyolefin MWD. Use of magnesium ethoxide support for polyethylene results in a narrower MWD than that obtained with a traditional titanium trichloride-triethylaluminium catalyst system[115]. Progressive addition of magnesium hydroxide to the former catalyst leads to molecular weight broadening[116]. In the case of propylene polymerization, supported catalysts are reported to narrow or broaden MWD depending on conditions[117]. The narrowing of MWD with supported catalyst is contrary to the expectations based on Thiele modulus criterion[118-120]. In view of the direct proportionality between Thiele modulus and the product of rate of propagation and concentration of active centres ($R_p . C^*$), supported catalysts should show appreciable broadening of MWD in comparison to traditional catalysts.

In addition to the catalysts, polyolefin MWD are dependent on polymerization conditions. Increased concentration of hydrogen (chain transfer agent) and increase in polymerization temperature leads to narrowing of MWD. Other parameters that have been found to influence polymer MWD are conversion, monomer and catalyst concentration, nature of diluent and residence time. MWD is also influenced by reactor design and configuration as well as mode of operation (batch or continuous). These considerations are discussed in section 5 of this review.

It is clear from the above discussion that a wide variety of techniques exists for control of MWD. However, these techniques are specific to the catalyst composition and reaction system in which they are used. It is therefore not possible to translate one MWD control technique from one catalyst or process to another although some general tendencies may be predictable. This severely limits the development of commercial catalyst systems, since for each new catalyst composition discovered, MWD control techniques must usually be developed before commercial exploitation becomes feasible. For propylene polymerization systems MWD control technique is considerably more difficult than with polyethylene. With high activity polyethylene catalyst activities are so high that there is a considerable leeway in tolerating any adverse effects of MWD control methods on catalyst efficiency. With polypropylene, however, the simultaneous requirement of high catalyst activity and high stereospecificity imposes severe restrictions on catalyst manipulation for MWD control purposes.

For polyethylenes, MWD is an important property which along with average molecular weight, density and short and long chain branching content determines its final properties and therefore its end applications. Broad MWD polyethylenes are used for blow moulding and pipe extrusion applications whereas narrow MWD polyethylenes are used for injection and rotational moulding and film applications.

For polypropylene, properties are essentially determined by average molecular weight and polymer crystallinity and MWD is relatively less important. However, it is found that for polypropylene narrowing MWD enables production of polymer with higher melt flow without sacrificing polymer properties[121]. However, this cannot be achieved now by the use of catalysts and is produced by controlled thermomechanical shear degradation of the polymer in an extruder using free radical initiators.

2.5.3 Crystallinity or stereoregularity

With prochiral alpha olefins such as propylene, the degree of stereoregularity of monomer placement determines polymer isotacticity and hence its crystallinity. The random sequence of insertion leads to atactic polymer which has little value as a thermoplastic. In the case of alpha or delta titanium trichloride a maximum of 90% isotactic index (determined as boiling heptane insolubles) can be obtained. Early in the evolution of Ziegler catalysts it was recognized that by addition of electron donors or polar adjuvants to the catalysts an increase in isotactic content could be obtained[19].

The mode of incorporating the donor into the catalyst has a profound influence on its performance. The methods often cited are: (a) addition to $TiCl_3$, (b) to preform a complex of donor with $TiCl_4$ and then reduce it with aluminium alkyl, (c) addition to a mixture of alkylaluminium and titanium tetrachloride, and (d) addition to aluminium alkyl. The addition method best suited for a system depends on the nature of catalysts and the Lewis base[122].

In propylene polymerizations, increase in catalyst activity is always accompanied by loss of stereospecificity. Consequently, with the development of high activity catalysts, the use of a Lewis base became a necessity. The current understanding of the role of internal and external Lewis bases (electron donors) has been discussed in section 2.4.4. Suffice to say that with the right choice and concentration of electron donors, chemists can now synthesize polypropylene of extraordinary steric purity.

2.6 Mechanism of polymer growth reaction

The mechanism of polymer growth reaction and the origin of regioselectivity and stereospecificity in olefin polymerization have been the subject of a number of recent reviews[11,26,123; 124]. The accumulated literature now favours a mechanism in which polymer growth occurs on the transition metal part of the catalyst which first gets alkylated by the alkylaluminium compound. The active site is envisaged as a titanium centre with both an alkyl substituent and a chlorine vacancy located on the edges of titanium trichloride crystal. Polymer growth occurs by complexation of the monomer on the vacant site followed by insertion of the polymer chain at the transition metal carbon bond. More recently a four step mechanism for olefin polymerization involving the intermediacy of a metallocyclobutane or metallocyclopentane has been proposed[125]. However, the validity of this mechanistic scheme has been questioned[126].

The unique regio- and stereospecificity of propylene polymerization has attracted considerable attention. It is now known that for isotactic polypropylene, insertion proceeds via a *cis* addition to the double bond and with high regioselectivity (greater than 95% 1,2). Based on elegant structural studies on olefin polymers, it is inferred that the active centre on catalyst should have chirality which enables favoured complexation of one prochiral face of the polymer over the other[122]. The precise factor which enables the catalytic centre to exercise such sharp selection is not known. Obviously an energy difference exists between transition states leading to an isotactic dyad or to a syndiotactic dyad which could be attributed to the steric and electrostatic interaction of the ligand monomer type as originally proposed for isotactic regulation on titanium chlorine surfaces[127,128]. The distinguishing features of isotactic and syndiotactic propagation of propylene are summarized in Table 8[124].

Table 8—Features of Stereospecificity in Alpha-Olefin Polymerization

	Isospecific propagation	Syndiospecific propagation
Addition of olefin to the M_t-C bond	*cis*	*cis*
Orientation of monomer during insertion	Primary C atom to metal atom	Secondary C atom to metal atom
Chiral centre determining stereocontrol	Metal ion of active centre	Last monomer unit of growing chain

3. Soluble Catalysts

3.1 Cyclopentadienyl derivatives of titanium or zirconium

Soluble catalysts based on titanium and zirconium cyclopentadienyls have attracted considerable attention in recent times[8,129-131]. Although high catalyst activities could be obtained for ethylene polymerization with Cp_2TiCl_2 or $Cp_2ZrCl_2/AlEt_2Cl$ or $AlEtCl_2$, the catalysts deactivated rapidly in solution, limiting its practical utility[132,133]. Sinn and **Kaminsky**[8] showed that the deactivation process can be overcome by addition of stoichiometric amounts of water to alkylaluminiums[134]. When water is added to trimethylaluminium in a 2:1 ratio, a cyclic oligomeric aluminoxane structure results, which appears to confer an unusually high degree of stability to the catalyst system.

Polymerization of ethylene with $Cp_2\,Zr\,(CH_3)_2/Me_3Al/H_2O$ has been well studied. At 90°C and 8 bar pressure in toluene diluent, a catalyst activity of $3\text{x}10^6$ g PE/g Zr.h. bar has been observed[135-137]. The following were the essential features of this reaction: (a) high rates are achieved at unusually high Al/Zr mole ratios ($\sim10^5$), (b) molecular weight inversely decreases with temperature with only oligomers produced at 100°C; however, rate increases linearly with temperature, (c) hydrogen can be used to regulate molecular weights, but its use reduces catalyst activity[113,138], (d) narrow molecular weight distribution polyethylenes (1.5-1.7) are generally produced, (e) with propylene, same catalysts produce exclusively stereoirregular atactic polypropylene, (f) π-indenyl derivative has a higher catalyst activity than cyclopentadienyl zirconium derivative[139], (g) homoleptic σ- alkyl derivatives of zirconium such as tetrabenzyl zirconium also show higher activity than π-cyclopentadienyl derivatives[137]. The possibility that such soluble catalysts may have structural similarities to supported high activity catalysts has been recognized[139]. Available kinetic data on ethylene polymerization is summarized in Table 9.

Such soluble catalysts are also active in copolymerization of ethylene with alpha-olefins. With 9% hexene-1, a density of 0.89 g/mL could be obtained (very low density linear polyethylene)[135]. EPDM terpolymers with ethylidene norbornene as diene monomer can also be obtained[140,141]. With $Cp_2Ti\,(CH_3)_2/Me_3Al/H_2O$ catalysts, a nearly alternating ethylene-propylene sequence was obtained[140]. Catalyst activities were high.

Table 9—Ethylene Polymerization Data Using Soluble Catalysts

Catalyst	Zr mol/L	Al mol/L	Time h	Temp °C	Press bar	Diluent	Activity kg/PE/ g Zr/h	Ref.
Cp_2ZrMe_2/Methyl aluminoxane	3.0×10^{-7}	4.3×10^{-3}	0.5	50	3	Heptane	320	139
$Zr(Benzyl)_4$/Methyl aluminoxane	3.1×10^{-7}	4.6×10^{-3}	0.5	50	3	Heptane	570	139
Cp_2ZrMe_2/Methyl aluminoxane	3.3×10^{-8}	2.2×10^{-3}	—	90	8	Toluene	24,800	137
Cp_2TiMe_2/Methyl aluminoxane	3.0×10^{-6}	5.0×10^{-3}	—	20	8	Toluene	4	137
Cp_2ZrCl_2/Methyl aluminoxane	3.0×10^{-8}	5.0×10^{-3}	—	70	8	Toluene	8,000	136
Cp_2ZrMe_2/Methyl aluminoxane	10^{-8}	1.58×10^{-2}	2	70	8	Toluene	4,500	136
$(Ind)_2Zr(CH_3)_2$/Methyl aluminoxane	3.48×10^{-7}	4.1×10^{-3}	0.5	50	3	Toluene	2176	139

In 1984, Ewen made a remarkable observation that ethylene bridged indenyl derivatives of titanium along with Me_3Al/H_2O (1:1) produced isotactic polypropylene[142]. This was the first report of isospecific propylene polymerization using a soluble catalyst with stereorigid chiral ligand. The existence of soluble catalysts with chiral centres has been previously alluded to in the literature. Using zirconium as metal instead of titanium gave improved results[131]. The essential features of propylene polymerization using such catalysts are (a) use of high Al/Zr ratios (10^4–10^5), (b) increasing catalyst activity with increasing temperatures, (c) decreasing molecular weights and isotacticity index with increasing temperatures (20°C, $\bar{M}w$=45,000, isotactic index =86%), and (d) narrow molecular weight distributions. Using optically active enantiomers of ethylene bis(tetrahydroindenyl) zirconium dichloride as catalysts, it was possible to obtain an optically active polypropylene from an achiral propylene monomer. This observation can be considered a watershed in the continuing evolution of the chemistry of stereospecific propylene polymerization. High regioselectivities, stereospecificities and stereoselectivities seem to be the distinctive features of homogeneous catalysts.

3.2 Soluble Mg-Ti catalysts

Recently interest has centred on soluble Mg-Ti catalysts for olefin polymerization. Soluble catalysts prepared by the reaction of magnesium octoate with titanium *n*-butoxide or magnesium chloride-2-ethylhexanol adduct with titanium *n*-butoxide or titanium chloride were effective for ethylene polymerization at 200°C[143]. The catalyst activities were moderate, i.e. 10-40 kg/g Ti (10 kg/cm^2). Addition of water improved catalyst activity. However, catalyst aging also improved catalyst activity in the absence of water[144]. In these cases no catalyst activity was observed with triethylaluminiums. Soga and coworkers[145] observed that propylene polymerization using soluble titanium *n*-butoxide/Et_2AlCl can be enhanced by addition of metal halide/2-ethylhexanol solution. Chlorides of metal ions with Pauling electronegativities below 9 acted as polymerization accelerators, the order being $CoCl_2 > MgCl_2 > MnCl_2 > NiCl_2$[145]. Unlike insoluble Mg-Ti catalysts, soluble analogs showed a rate curve which reached a stationary value during the course of polymerization. Such non-decay type kinetics for propylene has also been observed with an insoluble $MgCl_2$-$Ti(OBu)_4$-DEAC catalyst[146]. Titanium alkoxide supported on $MgCl_2$ also shows a relatively slower decay with ethylene polymerizations[57]. A soluble chromium *t*-butoxide-$MgCl_2$-2-ethylhexanol catalyst is reported to show high catalyst activity for ethylene polymerization (182 kg PE/g Cr/h, at 40°C, 1 h, 8 kg/cm^2 ethylene). The molecular distribution was very narrow[147].

3.3 Soluble vanadium catalyst

Recently, a highly active vanadium catalyst based on tris(2-methyl-1, 3-butanedionato) vanadium and Et_2AlCl has been reported which shows the characteristics of living coordination polymerization of propylene to syndiotactic polypropylene at −40°C in toluene[148]. The living polymer has been used to make a well-defined diblock copolymer of polypropylene with ethylene-propylene rubber.

4. Ziegler-Natta Catalytic Processes

Within three decades of the fundamental discovery of Ziegler-Natta catalysts, the processes using these catalysts have attained a considerable degree of maturity. In addition, the processes have witnessed continuous development to keep pace with the changing demands of improved catalysts, increased cost of energy and the sophisticated needs of the market in terms of new product properties with value added applications. Catalyst developments have had major impact on processes making a large number of operations down stream of reactor redundant. This is illustrated schematically in Fig. 4 for a typical polyolefin process. Process simplicity has attained a degree of technological plateau that it is hard to conceive of further simplifications. A typical polyolefin process of the future may well consist only of a reactor and a flashing vessel as essential process equipments.

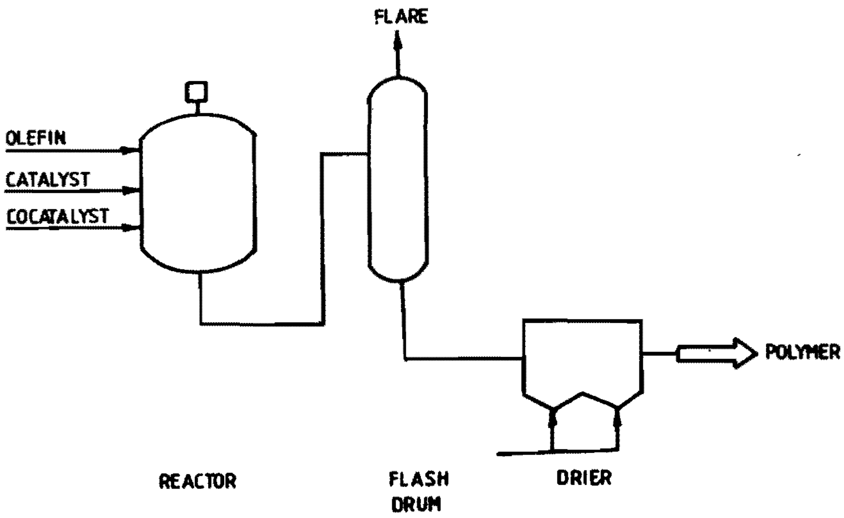


Fig. 4—Impact of catalyst development on process simplicity

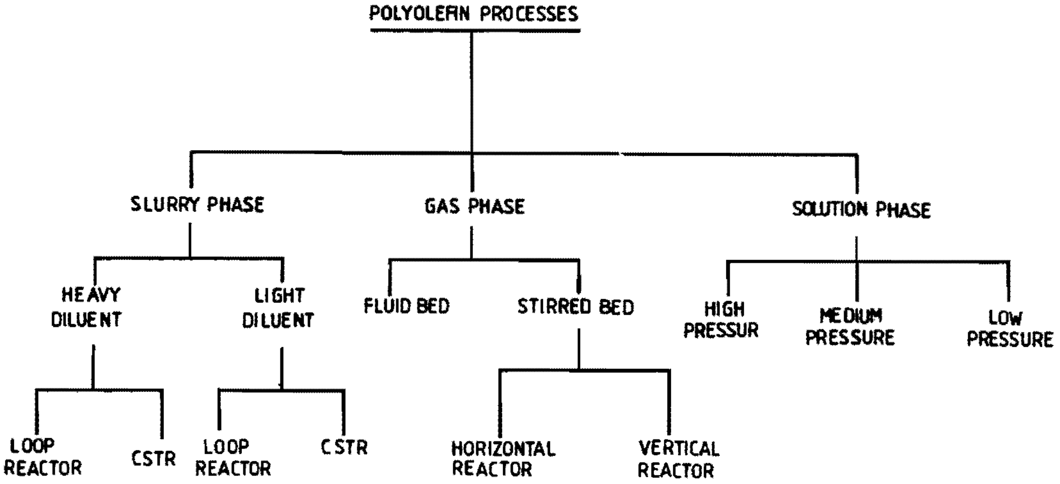


Fig. 5—Classification of commercial polyolefin processes

Table 10—HDPE Processes

	Slurry	Gas phase	Slurry	Solution	Solution
Process type	Particle form process using loop reactor	Fluidized bed	Liquid phase slurry autoclave	Liquid phase solution	Liquid phase in liquid ethylene, multizone autoclave, high pressure
Temperature, °C	85-105	85-100	70-90	180-270	150-300
Pressure kg/cm^2	7-35	20	7-10	50-200	7500
Residence time	1.5 h	3-5 h	2 h	2 min	30-40s
Solvent	Isobutane	None	*n*-hexane or isobutane	Cyclo-hexane	Hyper-critical ethylene
Comonomers	Hexene-1	Propylene Butene-1	Propylene Butene-1	Butene-1	Butene-1
Catalyst	1-3% chromic oxide on silica	Bis (triphenyl silyl) chromate on silica-alumina dialkylaluminium alkoxide	High activity Ziegler-Natta	Ziegler-Natta	Ziegler-Natta
Heat removal	Jacket cooling	Cooling of feed ethylene adiabatic reactor	Jacket cooling	Adiabatic reactor	Adiabatic reactor
Yield kg/g cat	5-50	4.0	10	4.4	5-6

Table 11—LLDPE Processes

	Solution	Solution	Solution	Gas phase
Process type	Liquid Phase/liquid ethylene, adiabatic multizone autoclave high pressure	Liquid phase solution low pressure	Liquid phase solution medium pressure	Gas phase fluid bed
Temperature, °C	150-300	130-180	180-270	85-100
Pressure, kg/cm^2	1100	25-30	100-150	20
Residence time,min	less than 1	5-20	2	180-300
Conversion,%, per pass	17-20	95	95	5
Diluent	Hypercritical ethylene	Hydrocarbon	Cyclohexane	None
Comonomer, % max	Butene-1,8-10, 4-Methyl Pentene-1	Butene-1, Octene-1, 4-Me-pentene-1	Octene-1,5 Butene-1,8-10	Butene-1, 9-10, Hexene-1
Catalyst	Ziegler	Ziegler, high activity	Ziegler low activity	Ziegler high activity or Cr-Ti on silica
Resin type	Pellet	Pellet	Pellet	Granular powder
Density	0.918-0.940	0.917-0.935	0.918-0.960	0.910-0.935

Table 12—Polypropylene Processes

	Slurry	Bulk	Gas phase	Gas phase
Process type	Liquid phase slurry-autoclave	Liquid phase slurry-autoclave or loop	Fluid bed	Agitated powder bed
Temperature, °C	70	50-60	50-88	80
Pressure, kg/cm^2	8-12	25-30	16-40	30
Conversion per pass, %	97	45	—	90
Residence time, h	2	2	—	1-2
Diluent	*n*-hexane	Liquid propylene	None	None
Catalyst	Ziegler-Natta (High yield-high selectivity)	Ziegler-Natta(High yield-high selectivity)	Ziegler-Natta(High yield-high selectivity)	Modified Ziegler-Natta (Medium yield)
Heat removal	Jacket cooling	Propylene reflux	Propylene gas specific heat	Partial evaporation of liquid propylene
Yield	300 kg/g Ti	300 kg/g Ti	20 kg/g cat	20 kg/g cat
Space-time Yield, kg.m^{-3}. h^{-1}	37.5	94	—	100
I.I% (Heptane insoluble)	96-98	94-98	95-98	95

Commercial polyolefin production processes based on Ziegler type catalysts can be broadly grouped as shown in Fig. 5. Each of the process types is in commercial operation. The essential features of these processes as applied to the three major polyolefins, viz. polyethylene, high density polyethylene, linear low density polyethylene and polypropylene are given in Tables 10-12.

Aspects of polyolefin processes have been well reviewed in a number of monographs[19,149-157] and recent publications[158-163]. The following sections will therefore deal with a brief description of process types with accent on more recent process changes related to continuing developments in catalysts.

4.1 Slurry phase processes

Slurry phase process constitutes one of the most commonly used process for the production of polyolefins. The reasons for its widespread use are : (i) relative simplicity of process operation, (ii) mild operating conditions, (iii) high conversions, (iv) high purity of product, (v) possibility of producing very high molecular weight resins, and (vi) easy heat removal. A typical flow scheme of a slurry phase process (high boiling hydrocarbon diluent, CSTR) using a highly active catalyst system is shown in Fig. 6. In view of the relatively long residence time encountered, such processes usually employ multiple reactors in series to optimise conversions and reactor volumes. In spite of this, the polymer space time yield is low, approx. 20-50 kg h^{-1}m^{-3}. In general, the conversion of ethylene to polyethylene is 98% while that of propylene to polypropylene is lower (~90%), requiring monomer recycle in PP processes. Complete monomer conversion as well as absence of diluent soluble byproduct in the case of polyethylene also

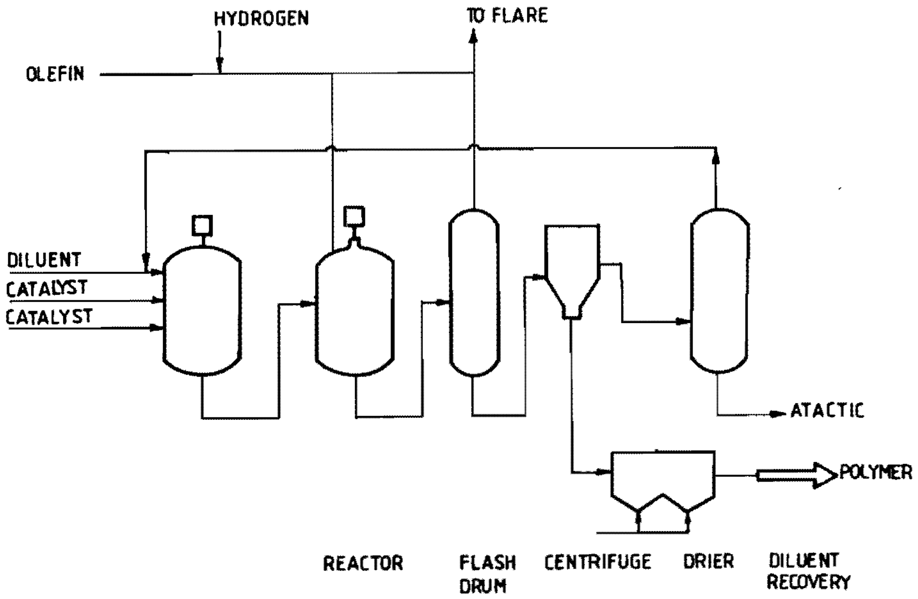


Fig. 6—Heavy diluent slurry process using high yield catalyst

enables direct recycle of a major portion of diluent back to the reactor without the necessity of purification and drying. Similar attempts to recycle diluent directly to reactor have also been made with PP process, but with lesser success as the diluent contains small amounts of atactic polymer which needs to be removed before it can be recycled. Process steps such as deactivation of catalysts and removal of catalyst residues from polymer no longer exist in view of the use of high activity catalysts for polymerization. With all catalysts left in, the final Ti content in the polymer is less than 10 ppm. However, the use of inert support in the catalyst preparation stage results in polymer with high ash content (about 100 ppm). However, for most applications, higher ash content is innocuous.

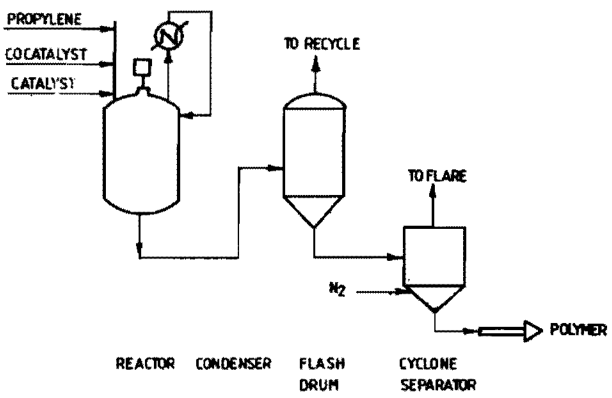


Fig. 7—Bulk or liquid pool process

The low boiling diluent process for polyolefins is similar to the heavy diluent process except for the diluent which is liquid propylene (in case of PP) and liquid isobutane (in case of HDPE). The main advantages of the process lie in the elimination of a diluent or its replacement with a diluent whose recycle is less energy intensive, complete absence of mass transfer limitations when polymerizing propylene in a pool of liquid propylene, and ease of polymer drying in the absence of high boiling diluent. A flow scheme for a typical low boiling diluent process is shown in Fig.7.

The process is characterized by higher polymerization rates resulting in better utilization of reactor volumes (space time yields of 75-100 kg $h^{-1}m^{-3}$). In a typical process slurry contents of 450-600 g/L are common. Heat removal is by a combination of jacket cooling and evaporative cooling by refluxing the low boiling diluent. Consequently the process operates at higher pressures relative to heavy diluent slurry process. The polymer slurry existing from the reactor is flashed to separate the polymer powder from the monomer, and recycled to the reactor. Polymer is dried with heated nitrogen. The process has no means of separating undesirable byproducts or catalyst residues and hence extensive washing and extraction sequences had to be incorporated when polypropylene was produced using this process and the conventional low yield catalyst. These additional steps vitiated the basic simplicity of the process. However development of high yield catalysts which require no atactic or catalyst removal has led to the resurgence of this process in recent years[117]. The major drawbacks of the inert diluent processes are (i) large inventory of hazardous hydrocarbon in the polymerization area, (ii) hazards associated with handling of dry polymer powder, (iii) greater chance of occurrence of runaway conditions in the reactor, and (iv) acknowledged propensity of the process to cause frequent fouling due to deposited polymer coating on the walls of process equipment caused as a result of the low volatility of the diluent.

The heavy diluent and light diluent slurry process is capable of producing a variety of alpha olefin copolymers. However, copolymerization of ethylene and higher alpha olefins (linear low density polyethylene) cannot be achieved in heavy diluent process because of copolymer solubility under process conditions. Intense efforts to develop a copolymer process in light diluent were reported a few years ago. However, no commercial process has been announced yet.

A variant of the slurry phase processes is the use of a vertical loop type reactor either with a heavy diluent or a light diluent. The process was pioneered by M/s Phillips Petroleum Company and was first commercialized for production of polyethylene (particle form-process). The process is currently used by both M/s Phillips (slurry in isobutane) and M/s Solvay et Cie (slurry in *n*-heptane). The Phillips catalysts are prepared by impregnating an aqueous solution of chromium trioxide (3%) with a high surface area (400-600 m^2/g) silica-alumina support. Control of molecular weight and molecular weight distribution is achieved by different techniques of catalyst activations. Polymerization occurs in a loop type reactor wherein the slurry is rapidly recirculated. With a given catalyst the polymerization temperature is the primary control for polymer melt index as Phillips catalysts are not susceptible to molecular weight control by use of conventional chain transfer agents such as hydrogen.

The loop reactor processes have found extension to polypropylene also. The Phillips process uses a loop reactor and liquid propylene as diluent and a conventional Ziegler catalyst comprising $TiCl_3$-Et_2AlCl. Monomer, catalyst, hydrogen as molecular weight modifier and a small amount of an antifouling chemical are fed into the reactor (Fig.8) where polymerization occurs. The resultant slurry is circulated through a reactor loop at about 20 ft/s by an axial flow pump. Reaction heat is removed by circulating water through jackets. The slurry is mixed with catalyst deactivating agents (acetylacetone or propylene oxide) in an agitated contactor and sent to a wash column where the polymer is washed countercurrently with liquid propylene. Liquid propylene from the top of the wash column is sent to recovery section where it is stripped free of catalyst residues and atactic polypropylene. The polymer powder is dried in a flash drier and sent for extrusion. The light diluent loop reactor process has all the advantages inherent to such processes, namely, high heat transfer coefficient, short residence time, low fouling characteristics and high space time yields (~200 kg $h^{-1}m^{-3}$). The recent announcement[164] of commercial processes for polypropylene using pipe (or loop) reactors in conjuction with high yield-high stereospecificity catalysts capable of both particle size and shape control has confirmed past predictions that loop reactors constitute one of the most optimum designs of polymerization vessels for polyolefins[158].

M/s Solvay et Cie also operate loop reactor processes in both light and heavy diluent for polypropylene: The process uses the proprietary Solvay catalyst (Table 3). The process, however, requires catalyst deactivation and atactic recovery steps.

4.2 Gas phase processes

The gas phase polymerization processes were commercialized in the late sixties and thus can be considered as relatively late starters in polyolefin process tech-

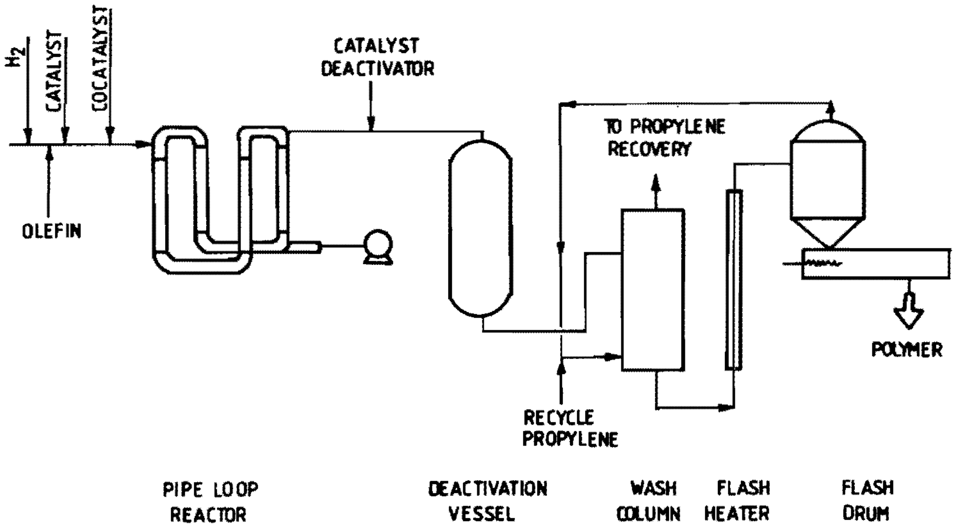


Fig. 8 — Liquid pool process using loop reactor

nology. The main obstacles were the inherent difficulties in designing and adequately controlling heterogeneous gas solid reaction systems and difficulties in controlling polymer properties. However, as understanding of these systems improved, considerable expansion in the use of gas phase processes for both polyethylene and polypropylene occurred. There are currently three basic types of gas phase polyolefin processes in commercial operation.

(a) The fluid bed process for linear low and high density polyethylene as commercialized by M/s Union Carbide and BP Chimie. Recently an extension of this process to polypropylene has been announced by Union Carbide and Shell[165,166].

(b) The vertical stirred bed process as first pioneered by BASF and further developed by M/s ICI and Northern Petrochemicals, USA[167].

(c) The horizontal stirred bed process as commercialized for polypropylene by Amoco Chisso[168].

These basic gas phase processes are described in the following sections.

4.2.1 *Fluid bed process*

The fluid bed process for polyethylene uses a variety of catalysts which contain chromium or titanium on silica magnesium containing supports (*vide infra*). The nature of catalyst controls polymer properties such as melt index, molecular weight distribution and density of polyethylene. Ethylene, hydrogen, comonomer such as butene-1 and dry catalyst powder are fed into the reactor continuously (Fig.9)[169,170]. Ethylene is circulated through the bed and through a disengagement section to permit separation of some of the fine particles from the gas. The circulating gas serves the multiple purpose of supplying monomer for the reaction, fluidizing and mixing the bed and providing a medium for heat removal. The average residence time of the particles in the bed is about 3-5 h during which time the particle grows to an average size of about 500 μm in diameter. Make up gas is fed to the bed at a rate equal to the rate at which polymer powder is withdrawn. The polymer is withdrawn into a discharge tank, where a small amount of accompanying ethylene gas is separated and sent to recovery. The polymer is then purged with nitrogen to free it from residual ethylene and sent to storage. Fluid bed processes offer substantial energy savings, are simple to operate and allow wide latitude in operating conditions and resulting product properties[170]. Catalysts are sufficiently active to require no catalyst removal steps. Molecular weight is controlled by chain transfer agents and reactor temperature. Molecular weight distribution and density are controlled by proper selection of the catalyst type. The fact that changes in catalysts are required to cover the full spectrum of polyethylene grades is one of the major drawbacks of fluid bed polyethylene processes.

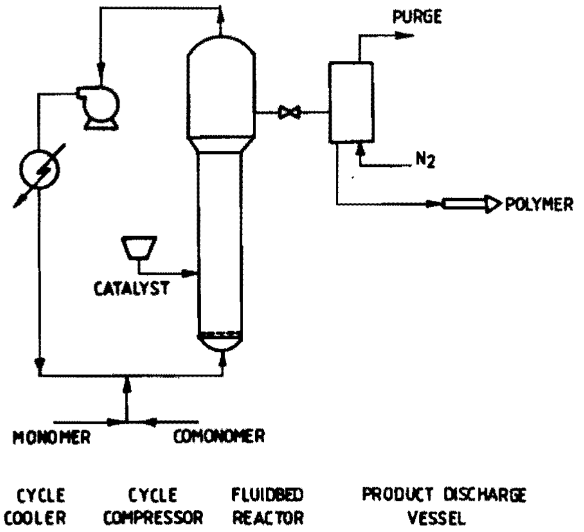


Fig. 9—Fluid bed gas phase process

4.2.2 *The vertical stirred bed process*

The vertical stirred bed gas phase process is employed by M/s BASF, W. Germany, for production of polypropylene. The process uses medium activity, high stereospecificity catalysts which require no atactic removal but require catalyst deactivation/dechlorination steps. Propylene is polymerized in gas phase in an agitated reactor to which the catalyst is added. The reactor contains a powder bed of polypropylene. The reaction heat is removed by direct contact cooling with liquid propylene. Propylene vapour is continuously reinjected into the reactor after condensation. Polypropylene powder is discharged intermittently into a cyclone from where residual propylene is flashed and sent to recovery. PP powder is further stripped with nitrogen. Use of chemicals such as propylene oxide and water in the extruder deactivates residual catalysts and reduces chlorine content in polymer[171]. The polymers produced from gas phase process have high ash content and titanium and chlorides in the 50 ppm range. The major hurdle in the full scale development of the gas phase process has been problems associated with reactor scale-up. Techniques of achieving uniform catalyst dispersion and efficient heat removal from a reactor full of polypropylene powder appear to be still in an evolutionary stage of development.

The process can also be used to produce polyethylene. The only difference is that the reactor is cooled by low velocity recirculating gas stream. Ethylene is expanded to the reaction pressure which results in a drop in temperature. As it rises through the bed, ethylene absorbs the heat of polymerization and leaves the bed at about 5°C below average polymerization temperature.

4.2.3 The horizontal stirred bed process

The horizontal stirred bed process for polypropylene is practised by Amoco Chemical Co., USA. The reactor is a horizontal cylindrical pressure vessel, stirred by paddles on an axial shaft. The lower part of the reactor is divided by weirs into four compartments[172]. Monomer and hydrogen are fed into each compartment from the bottom and catalyst is fed from the top. The mixture is continually stirred to avoid hot spots. As the polymer forms it passes from one section to the next and finally to an exit compartment. Reaction heat is removed not only by the recycling gas but by the addition and evaporation of liquid propylene. Amoco has developed its own medium activity catalysts (20 kg PP/g Ti/h, 97% isotactic) based on titanium and magnesium modified by a combination of esters and chlorosulphonic acids, which is employed in this process[173]. The process has the advantage of separately controlling the reaction temperature, gas feed compositions and catalyst concentrations in each of the compartments which lead to polymer with desirable properties. However, all the potential advantages of the process hinge on obtaining controlled bed uniformity which could present considerable engineering problems.

4.3 Solution processes

In solution process, polymerization takes place in a hydrocarbon solvent or in bulk monomer at a temperature above the melting point of the polymer. Processes of this type are in commercial use for the production of linear polyethylene by high pressure process, medium pressure processes, low pressure processes (Stamicarbon, Dow and Mitsui), propylene (Eastman Kodak) and poly(butene-1) (Shell). The main advantage of solution processes are that they can operate over a very wide range of temperatures and polymer properties (MW, MWD) can be controlled by temperature. Higher temperatures also imply higher reaction rates and very low residence time resulting in very high space time yields (1000-7500 kg $h^{-1}m^{-3}$).

4.3.1 High pressure process

A high pressure (1000 kg/cm^2) process for the production of linear low density polyethylene using Ziegler catalyst has been developed which is basically an extension of the conventional high pressure adiabatic multizone autoclave technology used for LDPE production[149,150]. The process is characterized by very short residence time (less than 2 min) and low conversion per pass (6-20%). Reaction heat is removed by cooling inlet monomer and the reactor is maintained in adiabatic conditions by balancing reaction heat with sensible heat to bring the inlet ethylene to reaction temperature. Under these conditions polyethylene is dissolved in ethylene. The catalyst used is highly active (60-145 kg/g Ti) and does not require removal. However, in view of low conversion per pass catalyst deactivation is required. The molten polymer is depressurized to remove unreacted ethylene and directly pelletized. The process has the advantage that it avoids use of solvent and polymer melting prior to extrusion. Polymer properties are controlled by adjusting reactor temperature and pressure and comonomer addition.

4.3.2 Medium pressure process

In this process ethylene and comonomer (C_3-C_8 alpha olefin) are dissolved in cyclohexane at 100 kg/cm^2, heated to a preset temperature and fed to an autoclave reactor. Catalyst used is a combination of titanium and vanadium halide in conjunction with a trialkylaluminium. The reaction temperature is controlled by adjusting the temperature of the feed stream. Polymer solution from the primary reactor is fed to a second reactor (tubular tail) wherein ethylene conversion is increased from 88 to 95%. At the exit of the tubular reactor chelating agents are added to complex unreacted catalysts and the catalyst residues are removed by adsorption on to activated alumina. Subsequently, the hot solution is flashed in two stages to remove most of the solvent and unreacted monomer and the melt is pelletized.

Polymer density is controlled by comonomer composition. Molecular weight and its distribution are controlled by adjusting reaction parameters such as temperature, hydrogen, catalyst and monomer concentration and the operating parameters of the tubular tail reactor.

4.3.3 Low pressure processes

In the low pressure processes (25-30 kg/cm^2), ethylene and comonomer are dissolved in a suitable diluent (normal or isoparaffins) and sent to a stirred reactor along with catalysts. Heat removal is achieved by cooling the feed to −40° C (Stamicarbon), refluxing the solvent (Dow) or by water circulation through jacket (Mitsui). The catalysts used in these processes are highly active and require no deactivation or removal from polymer. Polymer solution is continuously drawn off and sent to a flash drum. The unreacted ethylene, comonomer and diluent are flashed off in two stages and the molten polymer is pelletized. In some processes a second reactor is used to increase conversions.

4.3.4 Solution process for polypropylene

The solution PP process is one of the oldest processes and is generally considered obsolete. It is still used by Texas-Eastman for producing special coating grade resins. Propylene, catalyst and a high boiling hydrocarbon solvent are fed to a reactor at elevated temperatures. Feeds are precooled to enable the reactor to function adiabatically. The polymer solution is flash concentrated, and filtered to remove catalyst residues. The filtrate is cooled to precipitate isotactic fractions. The solid polymer is separated, extracted and again separated and dried. Combined solvent from various sections is stripped free of atactic polymer, purified and recycled. The process is similar in many respects to low pressure solution process for polyethylene. With a catalyst requiring no atactic separation or removal, the process is likely to have all the economic advantages of solution polyolefin process such as short residence time, use of polymerization enthalpy amd energy savings in powder melting prior to extrusion.

4.4 Catalyst developments

The greatest impetus behind new polyolefin process development is the continuing disclosure of high efficiency polymerization catalysts for olefins by a large number of polyolefin manufacturers[110,174-178]. The number of patents appearing in this area (approximately 400 per year) is a good indication of the level of industrial research activity. Large number of processes based on improved versions of the catalyst are already in operation especially for polyethylene and polypropylene. The precise compositions of catalysts used in commercial practice are highly proprietary. However, selected patents issued to some of the major polyolefin producers have been collected in Table 13 to enable appreciation of the complexity of the catalyst compositions and their performance under typical process conditions. The compilation is meant to be only illustrative and not exhaustive.

It thus appears as though catalyst development has reached a stage beyond which further improvements in activity and stereospecificity will show rapidly diminishing returns. However, further modifications to enable control of molecular weight distribution by manipulation of electron donor/support activation techniques[114], control of surface texture and shape of the polymer[179], incorporation of stabilizers and other additives to the polymer during its formation to facilitate eventual elimination of extrusion-pelletizing[180,181], and control of molecular weight without use of hydrogen can be expected.

5. Polyolefins Reactor Design and Engineering

Polyolefin polymerization processes use a wide variety of polymerization reactors whose detailed design is highly protected and often proprietary knowledge and not easily available in published or patented literature. In addition, olefin polymerizations exhibit some of the general characteristics of polymerization processes[182] such as high solution or slurry viscosities imposing an upper limit of reactor operation with regard to slurry content or melt index and high exothermicity, requiring considerable quantity of heat to be removed. Heat removal is made more difficult by the fact that high viscosities often result in heat transfer coefficients in stirred reactors being as low as k=25 W m^{-2} K^{-1}.

Other distinctive features of transition metal catalysed olefin polymerization processes which impose severe challenges to the design engineer are the extreme sensitivity of the process to impurities and the tendency to foul the reactor walls and agitator which have an adverse effect on heat transfer and consequently on the product quality. Similar to other polymerization processes, the desired product quality must be attained in the reactor itself and little opportunity exists for subsequent correction. Consequently, the objective of reactor engineering in a commercial polymerization reactor of a fixed size is to maximize reactor productivity at the desired product properties.

Broad guidelines for selecting the best type of reactor for a particular polymerization process has been described[183]. An elementary approach to process design of an ethylene polymerization is also available[184]. A review of selected reactor designs for olefin polymerizations as available in patent literature has been published[185].

In addition to the reactor, which forms the core of a polyolefin process, a number of down stream unit processes are also very significant and pose unique problems to the designer. These are degassing/centrifugation, extrusion, pneumatic conveying and the auxiliary solids handling systems as well as the diluent purification and recovery systems. A brief description of the complexities of some of the operations as well as design options have recently been discussed[159].

5.1 Reactor types and systems

The majority of polyolefin processes can be classified as occurring either in a diluent phase or gas phase. The diluent process employs a stirred vessel which is very versatile in view of its wide range of applications and excellent adaptability. The specific advantages of a stirred tank reactor and its process have been reviewed. These include suitability to both batchwise and continuous operation, ease of scale-up and standardized design. Major drawbacks are decrease in heat transfer area per unit reactor volume with increasing vessel size, difficulties associated with mass transfer, heat removal and agitation with increasing size of the vessel and difficulty of maintaining narrow residence time distribution during continuous operation. Also in

Table 13 — Representative Polyolefin Catalyst Compositions

No.	Patent No.	Company	Catalyst composition	Catalyst/product characteristics	Process type
	Polyethylene				
1	*US Pat* 3,976,632 (1976), *Chem Abstr*, **85** (1976) 143835s	Phillips	Titanium isopropoxide deposited on silica gel, calcined at 815°C and then impregnated with dibenzene chromium. Catalyst contains 2.5% Ti and 0.5% Cr	High melt index resins not possible with Cr on silica catalyst alone	Loop/ particle form
2	*Ger Pat* 857, 574 (1977) *Chem Abstr*, **89** (1978) 25087g	Phillips	Organomagnesium chloride is added to alkyl halide and alkyl aluminium compound followed by $TiCl_4$.Co-catalyst is triethyl-aluminium	10-60 kg/PE/g cat 300 to 6000 kg PE/g Ti	Loop/ particle form
3	*Ger Pat* 2,818,657 (1978) *Chem Abstr*, **90** (1979) 23993y	DuPont (USA)	Catalyst is a blend of $TiCl_4+VOCl_3$. Cocatalyst is $Al(iBu)_3+(nBu)_2Mg$	MI 0.2-100 g/10 min. d=0.915-0.965 g/cc Narrow MWD	Solution medium pressure
4	*Ger Pat* 2,522,331 (1975) *Chem Abstr*, **84** (1976) 90794y	DuPont (USA)	Tetrakisc (2-methyl-2-phenyl ethyl) zirconium (halogen and aluminium alkyl free)	High MW, high d (0.960 g/cc), catalyst productivity 15.5 kg/g cat.	Solution medium pressure
5	*Ger Pat* 2,350,782 (1974) *Chem Abstr*, **81** (1974) 121450c	CdF Chimie	$TiCl_3$-Et_2AlCl (Al/Ti=5) 240°C, 1600 kg/cm^2, 2 min contact time	d=0.930 g/cc	Solution, high pressure
6	*Ger Pat* 2, 439,775 (1974) *Chem Abstr*, **83** (1975) 11189h	CdF Chimie	Trimethylsilanol and trimethylaluminium was combined with $TiCl_3$ and 1-hexene in *n*-heptane suspension	Narrow MWD, catalyst productivity 2-3 kg/m mol Ti	Solution, high pressure
7	*Ger Pat* 2, 517, 567 (1975) *Chem Abstr*, **84** (1976) 74878y	Dow	nBu_2Mg, Et_3Al complex in Isopar E solvent is reacted with ethylaluminium sesquichloride to which is added tetraisopropyl titanate to give a solid catalyst	MI=2.5-12 g/10 min. Narrow MWD, High catalyst yield=172 kg/g. Ti h. kg/cm^2	Solution, low pressure
8	*US Pat* 4, 198, 315 (1980) *Chem Abstr*, 93 (1980) 95807h	Dow	Same as above but additionally containing nickel chloride	Broad MWD, catalyst yield 1000 kg/g Ti (150°C, 8 kg/cm^2, 20 min); d≤0.92 g/cc with octene-1	—
9	*US Pat* 4, 015, 059 (1977) *Chem Abstr*, **87** (1977) 6662k *US Pat* 4, 100, 337 (1978) *Chem Abstr*, **88** (1978) 90280k *US Pat* 4, 170, 589 (1979) *Chem Abstr*, **92** (1980) 23177b	Union Carbide	Silica activated at 250°C is treated with 5% $(NH_4)_2SiF_6$ and chromocene	Catalyst yield 345 kg/g Cr; d=0.956 g/cc at 95°C. 20 kg/cm^2	Gas phase fluid bed
10	*Ger Pat* 2, 802, 517 (1978) *Chem Abstr*, **89** (1978) 130183k	Union Carbide	Silica was impregnated with aluminium nitrate and then with tetraisopropyl titanate, dried, activated at 850°C and then treated with bistriphenyl silylchromate	d=0.949 g/cc, butene-1	Gas phase fluid bed

(Contd)

Table 13—Representative Polyolefin Catalyst Compositions—(*Contd*)

No.	Patent No.	Company	Catalyst composition	Catalyst/product characteristics	Process type
	Polyethylene				
11	*Ger Pat* 2, 609, 889 (1976) *Chem Abstr*,**85** (1976) 178428p *Ger Pat* 2, 742, 543 (1978) *Chem Abstr*,**89** (1978) 25092g	Union Carbide	Dry silica impregnated with chromocene and tetraisopropyl titanate, drying and treating with 0.3% $(NH_4)_2 SiF_6$ and then activating at 300-800° C	Catalyst yield 4900 kg/g Cr;d=0.920 g/cc (84° C,20 kg/cm^2)	Gas phase fluid bed
12	*Eur Pat Appl* 4, 645, (1979) *Chem Abstr*, **92** (1980) 42622g	Union Carbide	$TiCl_4$ and $MgCl_2$ are mixed in THF. Porous silica treated with triethylaluminium is impregnated with this catalyst mixture. Polymerization is performed in presence of additional triethylaluminium	Catalyst yield 500 kg/g Ti (85° C, 20 kg/cm^2) d=0.917-0.935 g/cc	Gas phase fluid bed
13	*Eur Pat Appl* 12, 147 (1980) *Chem Abstr*, **93** (1980) 187034z	Union Carbide	Catalyst prepared as above used to prepare terpolymers of ethylene with propylene-hexene-1. Instead of hexene-1,4-methyl pentene-1 or octene-1 can be used	d=0.915-0.930 g/cc. Catalyst yield 0.7-2.8 kg/g Ti	Gas phase fluid bed
14	*Jpn Pat* 57, 159, 806 (1982) *Chem Abstr*, **98** (1983) 107950k	Mitsui Petrochemicals	$MgCl_2$-2-ethylhexanol complex in decane is treated with $SiCl_4$ followed by $TiCl_4$ at 120° C. The solid catalyst obtained as above is used for polymerization in presence of triisobutylaluminium	Catalyst yield 400 kg/g Ti	Slurry in hexane
15	*Jpn Pat* 80, 151, 111 (1980) *Chem Abstr*, **94** (1981) 50914n	Mitsui Petrochemicals	$MgCl_2$ is ball milled with $TiCl_4$ and treated with $TiCl_4$ at 130° C for 2 h. The solid catalyst is used for polymerization along with triethylaluminium	Catalyst yield 573 kg/g Ti (80° C, 8 kg/cm^2, 3 h)	Slurry in hexane
16	*Ger Pat* 3, 124, 350 (1980) *Chem Abstr*, **98** (1983) 107962r	Hoechst	$TiCl_4$ and $Mg(OEt)_2$ are heated in a high boiling hydrocarbon to 90° followed by treatment with additional $TiCl_4$. The solid thus obtained was reduced with triisobutylaluminium and used for polymerization with isoprenylaluminium as cocatalyst	Catalyst yield 306 kg/g Ti	Slurry in hexane
	Polypropylene				
1	*Ger Pat* 3, 010, 871 (1981) *Chem Abstr*, **95** (1981) 204721g *Ger Pat* 3, 011, 236 (1981) *Chem Abstr*, **95** (1981) 220582t *Ger Pat* 3, 011, 273 (1981) *Chem Abstr*, **95** (1981) 204718m	BASF	A $TiCl_3$. 1/3 $AlCl_3$ catalyst modified with an ester or ether is used with DEAC cocatalyst modified with 2,6-di-*t*-butyl-*p*-cresol or other high molecular weight esters	Increased yield. Polymer isotacticity index is 97-99%	Gas phase

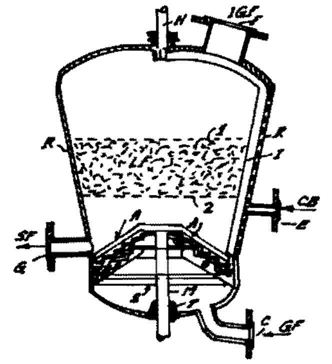
(*Contd*)

Table 13—Representative Polyolefin Catalyst Compositions—(*Contd*)

No.	Patent No.	Company	Catalyst composition	Catalyst/product characteristics	Process type
	Polyethylene				
2	*Ger Pat* 3, 010, 871 (1981) *Chem Abstr,* **95** (1981) 204721g	BASF	$TiCl_4$ treated with benzoyl chloride and then heated with magnesium ethoxide and used with TEA and ethyl *p*-anisate	—	Gas phase
3	*SAfr Pat* 80/2449 (1980) *Chem Abstr,* **94** (1981) 157358b	ElPaso	This patent describes the use of Montedison-Mitsui's high performance catalyst (FT-1) in ElPaso slurry in liquid propylene process	Catalyst yields are 375-400 kg polymer per g Ti at 66°C	Slurry in liquid propylene
4	*Eur Pat Appl* 2, 521 (1979) *Chem Abstr,* **91** (1979) 175972z	Phillips	$TiCl_4$, ethyl benzoate and magnesium or manganese chloride are milled in presence of propylene to prepare a solid compound which is used to polymerize propylene along with triethylaluminium and ethyl *p*-anisate	Catalyst yield is 155 kg/g Ti at 60°C/h. Isotacticity index=96.7% (xylene)	Slurry in liquid propylene
5	*Eur Pat Appl* 12, 397 (1980) *Chem Abstr,* **93** (1980) 205355m *US Pat* 4, 331, 558 (1982) *Chem Abstr,* **97** (1982) 92997j	Phillips	The catalyst support is formed by milling Mg or Mn chloride with an additive such as phosphite, phenol, ketone, silanol, carbonicacid ester or amine. It is then treated with $TiCl_4$ and used to polymerize propylene with triethylaluminium and ethyl *p*-anisate	Catalyst yield 700 kg/g Ti (12 kg/g cat) at 70°C/1.0 h. Isotacticity index: 93.7%	Slurry in liquid propylene
6	*Ger Pat* 2,643,143 (1977) *Chem Abstr,* **87** (1977) 68893x	Mitsui Petrochemicals Montedison	Anhydrous magnesium chloride and ethyl benzoate are ball milled and treated with $TiCl_4$ liquid at 80%-135°C. The solid catalyst is used to polymerize propylene in presence of triethyl aluminium. and ethyl *p*-anisate	Catalyst yield 113 kg PP/g Ti Isotacticity index=94%	Slurry in hexene
7	*Ger Pat* 3, 022, 738 (1981) *Chem Abstr,* **94** (1981) 122303n	Mitsui Petrochemicals	Anhydrous $MgCl_2$ is heated with decane and 2-ethylhexanol at 120°C and then treated with ethyl benzoate at 120°C and $TiCl_4$ at 0°C. The solid catalyst is used for polymerization with a mixture of triisobutylaluminium and ethylaluminium sesquichloride as cocatalyst and methyl *p*-toluate	Catalyst yield 428 kg/g Ti. Isotacticity index 98.4% (70°C. 7 kg/cm^2)	Slurry in hexane
8	*Belg Pat* 839, 131 (1976) *Chem Abstr,* **86** (1977) 172169d	Mitsui Petrochemicals	An adduct of $MgCl_2$. 6EtOH is treated with ethyl benzoate and $SiCl_4$ at 60°C followed by $TiCl_4$ at 130°C. The solid catalyst is used in conjunction with triethylaluminium and an electron donor	Catalyst yield 485 kg/g Ti. Isotacticity index 97.6%	Slurry in liquid propylene

continuous operation, a stirred tank reactor cannot achieve complete conversion like a batch reactor; continuous reactors connected in series are usually employed to improve monomer conversions. A variant of stirred tank for diluent phase polymerization is the pipe or loop reactor, originally introduced by Phillips Petroleum Company for the production of high density polyethylene[150]. Loop reactors have also been employed for production of polypropylene in both hydrocarbon and monomer diluent phases. A typical loop reactor used for the production of 1.7 tonne/h of polypropylene is constructed from a tubing of 50 cm internal diameter. Sections of tubing 15 m long were connected by 50 cm elbows to form a two-loop reactor with an internal volume of 100 m^3. In an example reported, the reactor was run at 49°C and 25 kg/cm^2 and with a flow velocity inside the reactor of 6 m/s. The solid content in the slurry was 35% and the average residence time of the reactors was calculated to be about 1.5 h. Baffles were used both before and after the impeller used to recirculate the slurry through the loop reactor. The baffles dampen out the vortex or cyclonic flow characteristics of the slurry as it is pumped.

In a loop reactor which may also adopt the form of a double loop, the residence time distribution of CSTR is approximated, when circulation is much greater than throughput. A high circulation rate prevents the formation of deposits and promotes good heat transfer. Whereas surface area of cooling jacket is of the order of 1-2m^2/m^3 of reactor volume (for a 40-50 m^3 reactor) for a stirred tank reactor[186], it can be thrice as much for loop reactor. This coupled with the fact that a loop reactor makes fuller use of its geometrical volume results in a high space time reactor productivity.



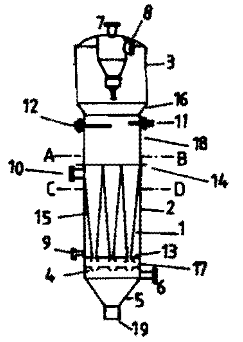
A. MOBILE PORTION
B. FIXED PORTION
M. DRIVING SHAFT
S. SUPPORT
R. REACTOR

C. ENTRY FOR FLUIDIZATION GAS
E. ENTRY FOR CATALYST INTRODUCTION
F EXIT OF FLUIDIZATION SOLIDS
G. EXIT FOR FLUIDIZATION GASES
I. SCRAPER
H. DRIVING SHAFT

Fig. 10—Stirred fluidized bed reactor for polyolefin manufacture

The gas phase polymerization reactors are a more recent entry into the commercial polyolefin scene and have attained a prominent status within a decade of their introduction. A variety of gas phase reactor designs are reported in the literature. The most common is a fluid bed reactor of the type commercially used by Naphtha Chimie and Union Carbide for the manufacture of linear polyethylenes[166]. A patented fluid bed reactor design of Montedison is shown in Fig. 10[187]. A fluid bed reactor design with a shell and tube heat exchanger[188] and a reactor having the ability to recover a polymer with controlled particle size[189] are also reported in the literature (Figs 11,12). BASF also has disclosed a fluid bed reactor design for polyolefins[190] (Fig. 13). A novel screw type gas phase reactor hs also been reported[191]. Horizontal gas phase reactors have been patented by Dart Industries (now Elpaso polyolefins) and Standard Oil Company of Indiana (Amoco[172]) (Fig. 14)

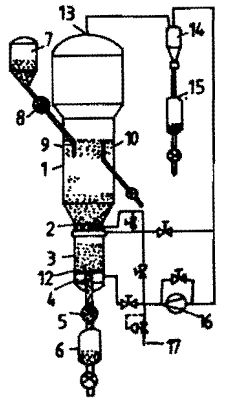
Adequacy of reactor design with regard to heat removal is important in view of the extreme sensitivity of polyolefin properties to reaction temperatures and the narrow temperature range within which transition metal catalysts offer optimum performance. All types of cooling are employed, namely direct cooling, indirect cooling and evaporative cooling[186]. Preliminary cooling of the feed by cooling the inlet reaction mixture (direct cooling) is employed in the production of polyethylene in stirred autoclaves under high pressures and in solution polymerization of ethylene at medium pressures. Owing to wall thickness of high pressure vessels, only a small fraction (about 5%) of the heat can be removed through walls. Cooling of the feed enables the reactor to be operated adiabatically.



1. CONICAL DIFFUSERS
2. COOLING SHEEL
3. EXPANSION CHAMBER
4. RECEIVER
5. COLLECTOR OF GRANULES
7, 8 ENTRY AND DISCHARGE PIPES FOR CYCLONE LOCATED INSIDE REACTOR
6. ENTRY FOR FLUIDIZATION GAS

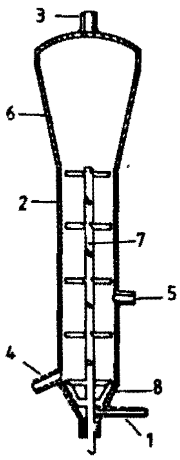
9,10 ENTRY AND DISCHARGE PIPES FOR COOLANT
11,12 CATALYST FEED PIPES
13,14 END PLATES
15 COOLENT CIRCULATING SPACE
16 ENTRAIMENT ZONE
17 GRID PLATE
18 REACTOR SHELL
19 DISCHARGE VALVE

Fig. 11—Shell and tube fluidized bed reactor for polyolefin production



1. REACTOR
2. DISCHARGE PORT
3. LOWER REACTOR
4. DISCHARGE PIPE
5. BUCKET WHEEL VALVE
6. POLYMER BIN
7. CATALYST DOSING TANK
8. CATALYST DOSING VALVE
9. CATALYST DOSING PIPE
10. DISCHARGE PIPE FOR FINE PARTICLES
11. FLUIDIZATION GAS
12. GRID PLATE
13. EXIT FOR FLUIDIZATION GAS
14. CYCLONE
15. DUST ACCUMULATOR
16. COMPRESSOR
17. MAKE UP MONOMER

Fig. 12—Fluidized bed polyolefin process featuring particles separation by size



1. MONOMER ENTRY PIPE
2. REACTOR
3. EXIT PIPE MONOMER
4. POLYMER DISCHARGE PIPE
5. CATALYST FEED PIPE
6. DISENGANGEMENT ZONE
7. AGITATOR
8. SCRAPER

Fig. 13-Fluidized bed polyolefin production reactor

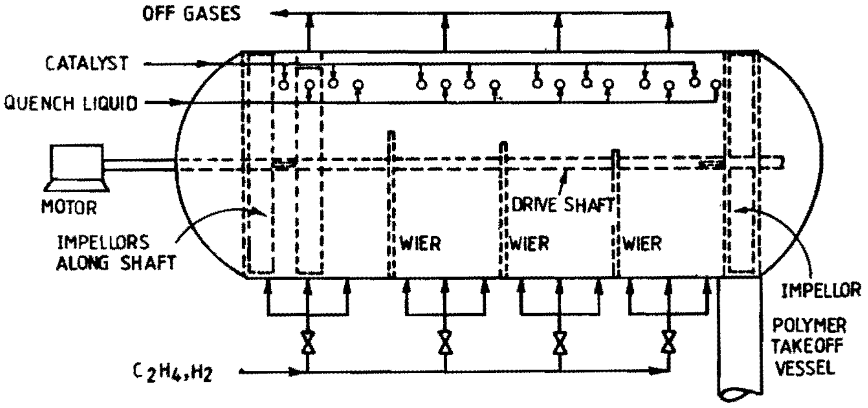


Fig. 14—Horizontal gas phase polymerization reactor

Cooling using a jacket is the most prevalent method of heat removal in polyolefin polymerization process. Internal cooling with water-cooled blade baffles or cooling elements or circulation of reaction mass through a pump and an external heat exchanger is ot very common on account of the fouling/plugging tendencies of the product slurry. This has effectively limited the maximum allowable sizes of commercial reactors. Evaporative cooling is employed in olefin polymerization conducted in low boiling diluents. However, this approach limits reactor filling capacity, causes fouling in overhead condenser and top shell of the reactor as a result of both physical carry over of polymer slurry and occurrence of polymerization due to carry over of catalyst component and its deposition in reactor top and overhead condenser. Agitator design also plays an important role in promoting heat transfer, avoiding hot spots and contributing to product homogeneity. Agitation criteria in polymerization reactors have been adequately reviewed[186,192].

Polyolefin polymerization reactors are normally provided with adequate safety controls to ensure a safe shutdown when runaway polymerization as a result of cooling water or agitator failure is observed. A network of coordinated and sequential emergency measures are automatically set in motion as soon as the temperature or pressure rises in the reactor. These include cutting of feed to reactor as well as catalysts, activation of emergency power supplies to cooling water pump or agitator, controlled let down and release of pressure through safety valves or rupture discs and introduction of suitable reagents which inhibit or destroy the catalyst activity[186].

5.2 Dependence of polymer properties on reactor design

Although all polyolefin properties are determined primarily by catalysts, they show substantial dependence on reactor operating variables, the responses of the reactor to these variables and the basic reactor design. Consequently these factors offer an additional mode of property control in olefin polymerizations. Attemtps have been made to correlate design parameters of a continuous stirred tank reactor for a polyolefin slurry process with the most important moments of the polymer MWD[193]. Residence time distribution dependence of MWD in continuous polymerization was studied by Bisenberger and Tadmor[194]. It has been found that it is possible to predict the MWD of polyethylene produced in a CSTR from batch reactor data by determining the effect of catalyst ageing on yield and molecular weights[195]. Enlargement of MWD by preventing backmixing and cycling the chain transfer agent in a CSTR has been reporetd[196]. Use of multiple CSTR in a cascade series with individual control of reactor operating parameters leads to broad and multimodal MWD.

5.3 Modelling and simulation of polyolefin processes

Process modelling and simulation of transition metal catalysed olefin polymerization pose a tremendous challenge and are still in an early stage of development[197,198]. This can be attributed to the - incomplete understanding of the factors controlling molecular weights, their distribution and stereospecificity, origin of catalyst aging or decay phenomenon, nature of active polymerization centres and the physical processes occurring within the pores and on the surface of catalysts. Relative importance of kinetics and monomer diffusion to active sites in determining the course of polymerization is still being debated[199]. Brockmeier and Rogan[200] have modelled the entire series of diffusion resistance based on a solid core catalyst model and concluded that kinetic resistance dominates in the very early stages of the polymerization, but it is quickly overtaken by the diffusion resistance associated with mass transfer of monomer through polymer shell. Modelling of both ethylene and propylene polymerization in which diffusion through the polymer is the controlling mass transfer resistance has been reported[197,198,200]. To account for catalyst particle disintegration by the growing polymer, models more complex than the solid core model have been developed and tested computationally with realistic parameters for heat and mass transfer[201]. Monomer concentration profiles for propylene as well as prediction of polymer rate, yield and molecular weight distribution have been made. Ray and coworkers have examined the kinetics of liquid and gas phase processes and have investigated intraparticle heat and mass transfer effects using a multigrain catalyst model[202-207]. Results show that in a slurry for high activity catalysts, external film mass transfer effects may be significant. For gas phase, monomer diffusion effects are critical at initial stages. Fragmentation and overheating phenomena occur at the same time scale. Thermal runaways leading to polymer melting and agglomeration are possible if heat transfer to the bulk phase is inadequate.

Laboratory research in olefin polymerization frequently employs a semibatch reactor[200,208]. An analysis of ethylene polymerization using a bubble column slurry reactor has been published[209]. Mathematical development of kinetic models has been reported which enables design of large scale continuous reactors from such semibatch laboratory reactors[210-212]. The models of a continuous reactor are derived from a semibatch model using equations appropriate for backmixing. Given inputs such as catalyst activity, stability, particle size and operating conditions such as temperature, pressure, reaction time and feed composition, these models can generate yield and production rates as outputs. In general, the effects of diffusion and catalyst decay cause yields from a continuous backmix reactor to be 25-30% lower than from a semibatch reactor at the same residence time. This yield penalty can be reduced by cascading backmix reactors in series which approach the behaviour of a plug flow continuous reactor and which is equivalent to a semibatch reactor. Extremely good correspondence between results from semibatch to continuous reactor have been obtained using such correlations. Practical benefits of modelling in problems relating to the design of catalysts, polymerization reactor design and control of the process have been recently reviewed[213].

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