A STUDY OF METHYLALUMINOXANE CATALYZED HOMOGENEOUS ZIEGLER-NATTA POLYMERIZATION OF ETHYLENE AND PHOTOPOLYMERIZATION OF ACRYLIC MONOMERS

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DEDICATED TO MY PARENTS

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DECLARATION

Certified that the work incorporated in thesis **"A Study of Methylaluminoxane Catalyzed Homogeneous Ziegler-Natta Polymerization of Ethylene and Photopolymerization of Acrylic Monomers"** submitted by Mr. S. Srinivasa Reddy was carried out by the candidate under my supervision, such material as has been obtained from other sources has been duly acknowledged.

S. Sivaram

(S. Sivaram)

Research guide

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ABSTRACT

This thesis presents results on the role of methylaluminoxane (MAO) in the coordination polymerization of ethylene initiated by zirconocene and free radical polymerization of methyl methacrylate initiated by light. The effect of preparative conditions on the properties of the MAO such as methyl/aluminum molar ratio, mol% TMA and average molecular weight are explored. The effect of these properties on the rate of ethylene polymerization and catalytic activity in combination with Cp_2ZrCl_2 at 70°C and one atmosphere ethylene pressure in toluene are reported. The results show that high molecular weight MAO ($\bar{M}n > 805$) with a methyl/aluminum molar ratio of 1.65 and 32.5 mol% TMA content is necessary to produce a high molecular weight poly(ethylene) with high catalyst activities and high initial rates of polymerization.

Monomeric sterically hindered aryloxy derivative of TMA, ($AlMe(BHT)_2$), was synthesized and found to be inactive for the polymerization of ethylene in combination with Cp_2ZrCl_2. However, upon addition of TMA to the Cp_2ZrCl_2-$AlMe(BHT)_2$ catalyst system, a kinetic profile similar to that of Cp_2ZrCl_2-MAO system is observed with low rates of polymerization and catalytic activity. Ethylene polymerizations were carried out for the Cp_2ZrCl_2-MAO and Cp_2ZrCl_2-TIBDAO catalyst systems at one atmosphere ethylene pressure under different conditions like concentration of Cp_2ZrCl_2, concentration of MAO/TIBDAO and temperature. Effect of these parameters on Rp, catalyst activity and molecular weight are reported. The beneficial effect of added trimethylaluminum (TMA) on changing the kinetic profile from a decay to a steady state type was demonstrated.

MAO has been found to initiate the photopolymerization of MMA with unusual features. A linear increase in number average molecular weight and conversion with time has been observed. This behavior is reminiscent of the "living" radical polymerization of MMA with thermal and photoiniferters and indicative of an environment where the free radical has unusual stability. Kinetic features of MAO initiated photopolymerization of MMA show significant difference from that of photopolymerization initiated by TMA. The actual initiating species in case of MAO induced photopolymerization is found to be the residual TMA present in MAO.

Experimental evidences has been provided to conclude that the mechanism of photopolymerization of MMA is a free radical process. Presumably Wittig "ate" type of complex acts as the initiating species. All evidences thus point out to the unusual stability of the growing free radical in presence of MAO. It is proposed that the growing radical is trapped within the cages of the MAO oligomer clusters. These cages, consisting of Al-O-Al linkages, are similar to other three dimensional structures such as, zeolites and γ-Al_2O_3.

GLOSSARY

$AlMe(BHT)_2$	Sterically hindered aryloxy derivative of TMA
BHT	Butylated hydroxy toluene
BMA	Butyl methacrylate
Cp	Cyclopentadienyl
Cp^*	Pentamethylcyclopentadienyl
DEAC	Diethylaluminum chloride
EAO	Ethylaluminoxane
EDTA	Ethylene diamine tetra acetate solution salt
Et	Ethylene
Flur	Fluorenyl
HIBTAO	Hexaisobutyltetraaluminoxane
Ind	Indenyl
IBAO	Isobutylaluminoxane
kp	Rate constant for propagation
kt	Rate constant for termination
MA	Methyl acrylate
MAO	Methylaluminoxane
MMA	Methyl methacrylate
PBMA	Poly(butyl methacrylate)
PE	Poly(ethylene)
PMA	Poly(methyl acrylate)
PMMA	Poly(methyl methacrylate)
PP	Poly(propylene)
PS	Poly(styrene)
TIBDAO	Tetraisobutyldialuminoxane
TNB	Titanium-n-butoxide
TIBAL	Triisobutylaluminum
TEAL	Triethylaluminum
TMA	Trimethylaluminum

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PART A

CHAPTER 1

HOMOGENEOUS METALLOCENE-METHYLALUMINOXANE CATALYST SYSTEMS FOR ETHYLENE POLYMERIZATION: A CRITICAL REVIEW

1.1 History

One of the most exciting and far reaching discoveries in polymer science and catalysis during the last forty years is the polymerization of olefins using transition metal based catalysts. Karl Ziegler was the first to discover that transition metal halides such as $TiCl_4$, $TiCl_3$, $ZrCl_4$, etc., in combination with alkylaluminum compounds convert ethylene to high molecular weight linear poly(ethylene)s[1]. Later, Natta independently discovered stereoregular polymers of α-olefins such as propylene, butene-1, and styrene[2]. Ziegler and Natta shared the 1963 Nobel Prize for this unique contributions to chemistry.

In view of their commercial importance, polyolefins have attracted significant interest from both industrial and academic laboratories towards development of newer combinations of catalysts. Major objectives in developing such catalysts are high catalyst efficiency and high stereo specificity. Highly efficient supported catalysts with catalyst activities in the range of 300 - 500 Kg/g-atom metal, and high efficiency homogeneous metallocene/aluminoxane catalyst systems which give high activities, narrow molecular weight distribution polymers and good stereochemical control are some of the major achievements in recent years. Table 1.1 provides a glimpse of the chronological development in this area since the initial discoveries of Ziegler and Natta.

1.2 Classification of Ziegler-Natta catalysts

Both basic and commercial interests in developing newer combinations of Ziegler-Natta catalysts have prevented the emergence of a simple classification of these catalysts. Boor defined these catalyst systems as products formed from reactions involving certain transition metal compounds of Group IV-VII[3], such as Ti, V, Cr compounds with alkyl or aryl halides of Group I-III. Further developments like supported high activity catalysts, metallocene-methylaluminoxane (MAO) catalysts and the like do not fall within the scope of the above definition. The most convenient method of classification of these catalysts is as follows.

Table 1.1 Chronology of Development in Ziegler-Natta Catalysis

Year	Catalyst System	Polymer	Activity (Kg-Polymer/g-metal.h)	Tacticity (%)
1953 - 55	$TiCl_4$ - Et_3Al	Polyethylene	10 - 15	-
		Polypropylene	5 - 10	50 - 60
	$TiCl_3$ - Et_3Al	Polyethylene	5 - 10	-
		Polypropylene	1 - 3	60 - 80
1955 - 60	Electron Donors. $TiCl_3$ -Et_3Al	Polyethylene	-	-
		Polypropylene	1 - 10	90 - 95
1970 - Present	Supported $MgCl_2$.$TiCl_4$ - Et_3Al	Polyethylene	500 - 1000	-
		Polypropylene	500 - 1000	50 -70
	Supported $MgCl_2$.Electron Donor.$TiCl_4$ - Et_3Al	Polyethylene	500 - 1000	-
		Polypropylene	300 - 500	90 - 99
1980 - Present	Homogeneous Metallocene - Methylaluminoxane	Polyethylene	400 - 500	-

Contd....

Table 1.1 Contd....

Year	Catalyst System	Polymer	Activity (Kg-Polymer/g-metal.h)	Tacticity (%)
1985 - Present	Stereorigid Metallocene - Methylaluminoxane	Polypropylene	150 - 170	96 - 98
	Homogeneous Aluminum Free Metallocene catalysts	Polypropylene	0 - 1	97 - 98
	Supported metallocene catalysts/AlR_3 or MAO	Polypropylene	10-20	80-90
1986 - Present	$Ti(OR)_4$ - MAO	Syndiospecific polystyrene	0.4 - 0.5	80-96
	$CpTi(OR)_3$ - MAO		3300	82
	$Mg(OH)_2/Ti(OBu)_4$ - MAO		0.3	100
1988 - Present	Cp_2ZrCl_2 - MAO	Ethylene - Propylene copolymer	50 - 100	Aspecific
	$Et[IndH_4]_2ZrCl_2$ - MAO		5 - 15	Isospecific
	i-Pr(Cp)(Flu)$ZrCl_2$ - MAO			Syndiospecific
	Cp_2ZrCl_2 - MAO	Ethylene - Hexene copolymer	-	Aspecific
	$Et[IndH_4]_2ZrCl_2$ - MAO			Isospecific
	i-Pr(Cp)(Flu)$ZrCl_2$ - MAO			Syndiospecific
1988 - Present	$Et[Ind]_2ZrCl_2$ - MAO	Ethylene - cyclic olefin copolymers	0.02 - 0.14	-

1.2.1. Heterogeneous Ziegler-Natta catalysts
1.2.2. Homogeneous Ziegler-Natta catalysts

It should be emphasized that these terms imply only the physical state of the catalysts and not the polymerization reaction as a whole.

1.2.1 Heterogeneous Ziegler Natta catalysts

Heterogeneous Ziegler-Natta catalysts are the industrially successful polymerization catalysts. These catalysts can be divided into unsupported and supported ones. $TiCl_3$ is a successful unsupported heterogeneous Ziegler-Natta catalyst. Natta's extensive work on this catalyst system revealed that only a very small percentage of the Ti in $TiCl_3$ participates during polymerization. This recognition eventually lead to the development of supported catalysts[4]. The ability to achieve high catalyst efficiencies has dramatically improved the economics of polyolefin process by eliminating all steps associated with catalyst removal and solvent purification/recovery. The most commonly used support is based on anhydrous $MgCl_2$. It is generally believed that the support plays an inert role in the polymerization mechanisms[5,6]. $MgCl_2$, is found to be the best support material due to similarities in atomic size, shape and coordination number between Mg and Ti[7].

1.2.2 Homogeneous Ziegler-Natta catalysts

Discovery of homogeneous bis(cyclopentadienyl)titanium(IV)dichloride (titanocene) - alkylaluminum catalyst system by Breslow and coworkers for ethylene polymerization kindled considerable interest in the area of soluble catalyst for olefin polymerization[8]. However, for over twenty years homogeneous catalysts did not attract wide spread interest because of poor catalyst activity, short kinetic life time and lack of stereospecificity. The recent discovery of homogeneous, highly active and stereospecific metallocene-MAO catalysts[9] and cationic metallocene based single component catalysts have stimulated renewed commercial and scientific interest in homogeneous catalysts[10]. In a homogeneous catalyst every active center is equally reactive thereby producing a Schultz-Flory distribution of molecular weights. Homogeneous catalysts can be divided conveniently into two classes.

1.2.2.1. Homogeneous Ziegler-Natta catalysts based on alkyl aluminum/aluminoxane as cocatalyst

1.2.2.2. Cationic Metallocene based single component catalysts

1.2.2.1 Homogeneous Ziegler-Natta catalysts based on alkyl aluminum/ aluminoxane as cocatalysts

A wide variety of homogeneous Ziegler-Natta catalysts based on alkyl aluminum as cocatalysts are reported in literature for polymerization of olefins. Most commonly, Ti, V, Cr, and Ni based transition metal catalysts in conjunction with alkylaluminums are used as homogeneous catalysts. Cr based homogeneous catalysts are well known for diene polymerization studies[11]. Ni based homogeneous catalysts are good ethylene oligomerization catalysts[12]. For α-olefin polymerization, metallocenes and V compounds in conjunction with alkylaluminums are reported. These homogeneous polymerization catalysts based on alkylaluminums can be subdivided into two categories.

a) Vanadium based catalysts
b) Metallocene based catalysts

a) Vanadium based homogeneous Ziegler-Natta catalysts

Vanadium based catalysts in combination with alkylaluminums have been well studied for the polymerization of propylene. They lead to highly syndiospecific PP at temperature below -60°C[13a,13b]. These catalysts are also used for polymerization of higher α-olefins and copolymerization of ethylene with higher α-olefins[13c-f]. It is observed that as temperature increases the polymerization becomes nonstereospecific. This factor has limited the commercial development of this catalyst system for stereospecific polymerization. However, these catalyst systems can be used to prepare a large number of homo, block, random and alternating polyolefins.

b) Metallocene (Ti and Zr based) based Ziegler-Natta catalysts

Breslow and Newburg were the first to identify that a solution of bis(cyclopentadienyl)titanium(IV)chloride in presence of alkylaluminums exists as a homogeneous clear solution[14] capable of polymerizing ethylene to reasonably high molecular weight poly(ethylene)s. Later studies by Natta et al[15]., Chien et al[16a,b]., Patat[17], Patat and Sinn[18], Shilov et al[19]., Adema[20], Clauss and Bestian[21], Dyachkovski[22], Henrici-Olive and Olive[23] Reichert[24], Kaminsky[25], Waters and Mortimer[26], and Mejlik[27] have contributed to our significant understanding of olefin polymerization using homogeneous Ziegler-Natta systems by suitably modifying the catalyst and cocatalyst components. The salient features of ethylene polymerization using Ti or Zr based metallocene/alkylaluminums catalysts are summarized in Table 1.2. These catalysts show low to medium activities, narrow molecular weight distribution and rapid deactivation of catalyst leading to formation of an inactive species. The process of deactivation was studied by kinetic and spectroscopic techniques. It was shown that +4 oxidation state was an active species during polymerization of ethylene. The lifetime of the active species is very short because of rapid deactivation process[8,28] due to side reactions such as alkyl exchange, H-exchange and reduction (Figure 1.1.). The intermediate complexes due to these side reactions were isolated and spectroscopically characterized in Ti and Zr systems[8,28]. The major side reactions in both Ti and Zr based metallocene catalysts in combination with alkylaluminums are schematically represented in Figures 1.2 and 1.3.

It is well known that ethylene insertion into the active [M]-C is a prerequisite for the rapid propagation step. Dyachkovski[22] and co-workers based on kinetic measurements, showed that the insertion takes place on a titanium cation of type

Table 1.2 Polymerization of Ethylene using Various Homogeneous Ziegler-Natta Catalysts

Catalyst system	Polymerization conditions	Activity (g-PE/g-Ti)	Features	Reference
$Cp_2TiCl_2/Et2AlCl$	Ti = 10 mmol/L, Al/Ti = 4, temperature = 30^0C, pressure = 3.4 bar	-	$\bar{M}w/\bar{M}n = 3.6$, $[\eta]_{red} = 2.6$ dL/g	14b
$Cp_2TiCl_2/Me2AlCl$	Ti = 4 mmol/L, Al/Ti = 2.5, temperature = 15^0C, pressure = 1.32 bar.	530	$\bar{M}n = 8800$, $[\eta]_{sp} = 0.76$ dL/g	16a
$Cp_2TiEtCl/EtAlCl_2$	Ti = 3 mmol/L, Al/Ti = 2, temperature = 20^0C, [M] = 0.10 mol/lit., time = 1.25 min.	134	-	27
$Cp_2TiEtCl/EtAlCl_2$	Ti = 10 mmol/L, Al/Ti = 1, temperature = 0^0C, Pressure = 1 bar, toluene, time = 40 min	-	$\bar{M}w/\bar{M}n = 1.55$,	26
$Cp_2TiEtCl/EtAlCl_2$	Ti = 0.24 mmol/L, Al/Ti = 1.5, temperature = 20^0C, benzene	1010	$\bar{M}v = 95000$, $[\eta] = 2.1$ dL/g	88

Contd....

Table 1.2 Contd....

Catalyst system	Polymerization conditions	Activity (g-PE/g-metal)	Features	Reference
$Cp_2ZrCl_2/AlMe_3$	Zr = 0.0058 mmol/L, Al/Zr = 870, temperature = 50^0C, pressure = 4 bar, time = 1 h, toluene	38,700	viscosity = 2.6 dL/g	87
$^{\bullet}Cp_2ZrCl_2/AlMe_3$	Zr = 0.0058 mmol/L, Al/Zr = 870, temperature = 50^0C, pressure = 4 bar, time = 1 h, toluene	155,400	viscosity = 2.6 dL/g	87
$Cp_2ZrCl_2/AlEt_3$	Zr = 0.0058 mmol/L, Al/Zr = 870, temperature = 50^0C, pressure = 4 bar, time = 1 h, toluene	2,100	viscosity = 1.4 dL/g	87
$^{\bullet}Cp_2ZrCl_2/AlEt_3$	Zr = 0.0058 mmol/L, Al/Zr = 870, temperature = 50^0C, pressure = 4 bar, time = 1 h, toluene	140,700	viscosity = 5.2 dL/g	87
$Cp_2ZrCl_2/AliBu_3$	Zr = 0.0085 mmol/L, Al/Zr = 590, temperature = 50^0C, pressure = 4 bar, time = 1 h, toluene	6,900	-	87

Contd....

Table 1.2 Contd....

Catalyst system	Polymerization conditions	Activity (g-PE/g-metal)	Features	Reference
$^{\bullet}Cp_2ZrCl_2/AliBu_3$	Zr = 0.0085 mmol/L, Al/Zr = 590, temperature = 50^{0}C, pressure = 4 bar, time = 1 h, toluene	1,014,000	viscosity = 8.4 dL/g	87
$^{\bullet}Cp_2Zr(OH)_2/AliBu_3$	Zr = 0.00058 mmol/L, Al/Zr = 8700, temperature = 50^{0}C, pressure = 4 bar, time = 1 h, toluene	929,200	viscosity = 9.8 dL/g	87
$Cp_2ZrMe_2/AlMe_3$	Zr = 0.004 mmol/L, Al/Zr = 526, temperature = 50^{0}C, pressure = 4 bar, time = 1 h, toluene	4,175	viscosity = 2.6 dL/g	61a
$Cp_2ZrPh_2/AlMe_3$	Zr = 0.0067 mmol/L, Al/Zr = 750, temperature = 50^{0}C, pressure = 4 bar, time = 1 h, toluene	5,425	viscosity = 3.3 dL/g	61a
$Cp_2Zr(CH_2Ph)_2/AlMe_3$	Zr = 0.0063 mmol/L, Al/Zr = 800, temperature = 50^{0}C, pressure = 4 bar, time = 1 h, toluene	8,400	viscosity = 2.7 dL/g	61a

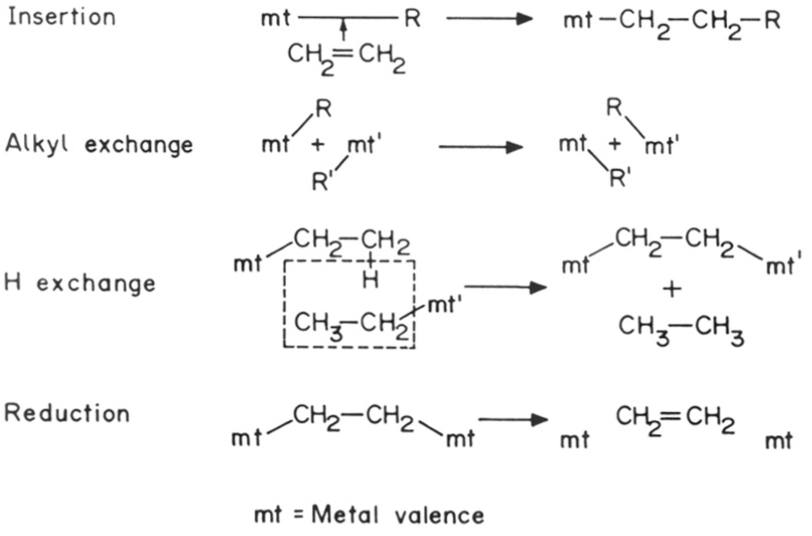


Fig. 1.1 Reactions involved in homogeneous catalysts

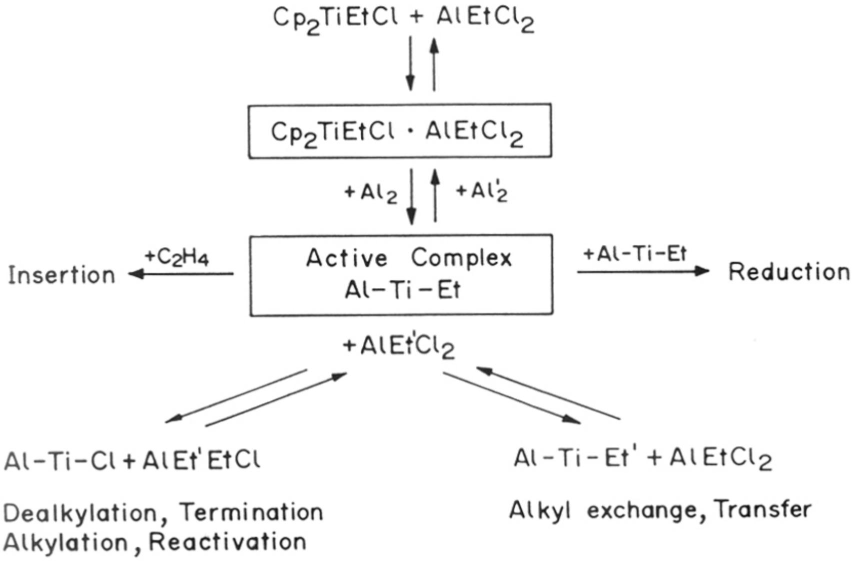


Fig. 1.2 Reactions in a soluble titanium system

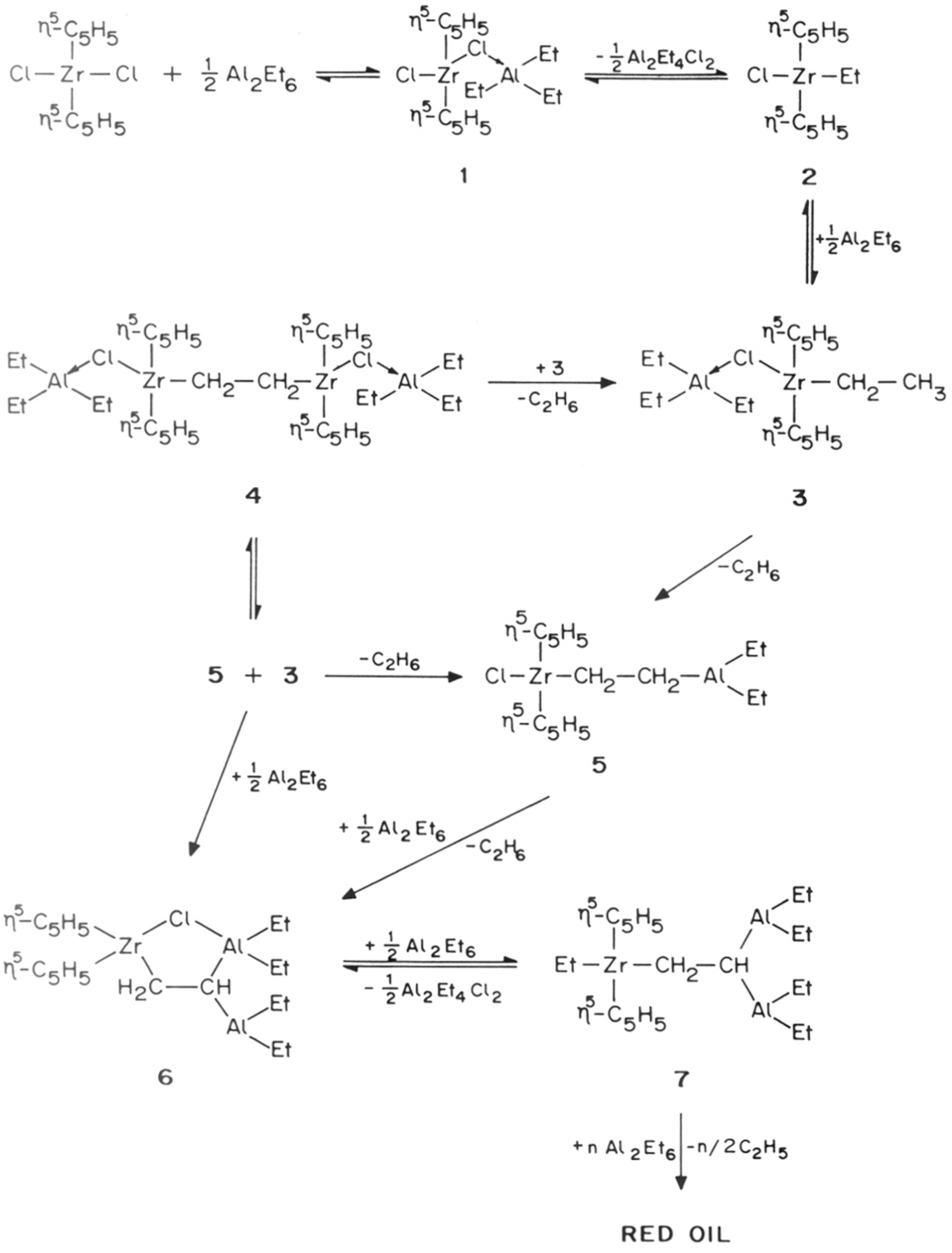
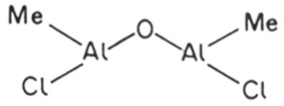


Fig. 1.3 Reactions in a soluble zirconium system

$(C_5H_5)_2Ti^+$-R for the catalyst system $Cp_2TiRCl + AlRCl_2$. Thus, on account of these severe side reactions, unfavorable kinetics, and low polymerization activities, titanium based metallocenes did not achieve great success. A number of attempts were made to improve these catalysts. Reichert and Meyer were the first to show an enhancement in polymerization activity upon addition of water to the $Cp_2TiEtCl/AlEtCl_2$ catalyst system[24,29]. Breslow and Long obtained considerable increase in activity and molecular weight for ethylene polymerization with the catalyst system $Cp_2TiEtCl_2/AlMe_2Cl$ by increasing the amount of water to ratios of 3/1(Al/H_2O) and 2.5 (Al/H_2O)[30]. Sinn and Kaminsky observed a large increase in activity, upto 500,000 gPE/gTi, when a halogen-free soluble catalyst system, Cp_2TiMe_2 was added to two equivalents of trimethylaluminum (TMA) or triethylaluminum (TEAL) previously treated with one equivalent of water[31]. Mejlik and coworkers also reported that soluble catalysts, $Cp_2TiEtCl/AlEtCl_2$ show an increase in activity when water is added to the system[27,32]. Literature data on the effect of water on polymerization of ethylene using various homogeneous Ziegler-Natta catalysts is summarized in Table 1.3.

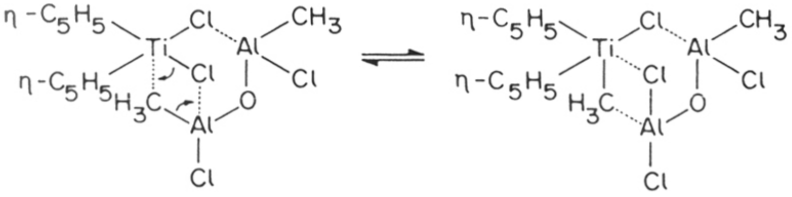
Based on polymerization results, Breslow and Long postulated a bridged structure for the complexes formed between $AlMe_2Cl/H_2O$



Further, it was shown that these bridged structures on reaction with Cp_2TiCl_2 generated a stabilized complex. This complex showed high activity in comparison with active species formed in the absence of H_2O for the polymerization of ethylene.

Table 1.3 Effect of Water on Polymerization of Ethylene using Various Homogeneous Ziegler-Natta Catalysts

Catalyst system	Water:Alkyl Al (mol ratio)	Polymerization conditions	Activity (Kg-PE/mol-Ti.h.atm)	Features	Reference
$Cp_2TiMe_2/AlMe_3$	-	Ti = 2 mmol/L, Al/Ti = 7.5, temp. = -10^{0}C, pressure = 3 bar, time = 2 h	1.1	yield = 12.9 g/lit	28
$Cp_2TiMe_2/AlMe_3/H_2O$	0.5	Ti = 0.07 mmol/L, Al/Ti = 2000, temp. = 21^{0}C, pressure = 7 bar, time = 1.5 h	48	yield = 36 g/lit	28
$Cp_2TiCl_2/AlMe_2Cl$	-	[Ti]:[Al] = 1:2.5 to 1:6, temp. = 30^{0}C	40-200	-	30
$Cp_2TiCl_2/AlMe_2Cl/H_2O$	0.5	[Ti]:[Al]:[H_2O] =1:6:3, temp. = 30^{0}C	2000	-	30
$Cp_2TiEtCl/AlEtCl_2$	-	Ti = 0.75 mmol/L, Al/Ti = 2, temp. = 0^{0}C, time = 2 h	1.1 [P]/Ti atom [p]= concn. macromolecule	$\bar{M}w/\bar{M}n = 4$, $\bar{M}n= 7,900$	27
$Cp_2TiEtCl/AlEtCl_2/H_2O$	0.5	Ti = 0.75 mmol/L, Al/Ti = 2, temp. = 0^{0}C, time = 2 h	0.15 [P]/Ti atom [p]= concn. macromolecule	$\bar{M}w/\bar{M}n = 2.$, $\bar{M}n =5,70,000$	27
$Cp_2TiEtCl/AlEtCl_2$	-	Al/Ti = 8	-	Kp = 7.2 Lit/mol.s, E_A = 7.9 kcal/mol	27
$Cp_2TiEtCl/AlEtCl_2/H_2O$	0.5	Al/Ti =15	-	Kp = 290 L/mol.s, E_A = 5.2 kcal/mol	27



Stabilized complex

Mejlik and co-workers performed kinetic studies using $Cp_2TiEtCl/AlEtCl_2$ catalyst system and postulated that the activation effect of aluminoxanes is not connected with an increased number of active sites, but rather with an extraordinary increase of the rate constant of chain propagation, kp. Sinn and Kaminsky studied extensively the reaction between AlR_3 and water to understand the high polymerization activity of metallocene in presence of H_2O/AlR_3. In the course of these studies, they observed that an oligomeric aluminoxane was formed by the reaction of TMA and water[8] (Equation 1.1)

$$nAl(CH_3)_3 + nH_2O \text{ ------> } [\text{-}Al(CH_3)O\text{-}]_n + 2\,nCH_4 \qquad (1.1)$$

which was responsible for high polymerization activities. These oligomeric species are formed by elimination of methane gas. Aluminoxanes thus produced are soluble in hydrocarbons and contain 5 - 28 aluminum atoms per oligomer. When these aluminoxanes are used as cocatalysts, activities upto 10^6 gPE/g-metal could be achieved with metallocene as catalysts for the polymerization of ethylene. This major discovery generated a significant interest in this area of olefin polymerization chemistry. This can be evidenced by a large number of patents issued to different companies during the last 10 years. The major advantages of these homogeneous metallocene-aluminoxane catalysts are a) high catalyst activity b) low catalyst requirements c) ability to polymerize a wide variety of monomers by suitably tuning the ligands around the transition metal d) narrow molecular weight distribution approaching the theoretical value of 2.0 as predicted by Schultz-Flory mechanism and e) ability to polymerize α-olefin with almost any desired stereospecificity. However the catalyst system is not without its disadvantages. These are a) a decay type kinetics with ethylene/higher α-olefin b) high Al/Zr ratios for obtaining high catalyst activity and relatively stable kinetic profile. c) high cost of MAO d) inability to adopt the catalysts to processes operating in slurry or gas phase and e) poor control over polymer morphology.

1.2.2.2 Cationic Metallocene based single component catalysts

The metallocene-aluminoxane catalyst system has implicated the unsaturated cation like metal center [Cp_2MR^+] as an active center during polymerization[33]. Different indirect studies such as NMR[34], XPS[35], electrodialysis[36], chemical trapping[37] and theoretical studies[38] have supported this hypothesis. Recently success has been achieved in isolation and characterization of aluminum free cationic metallocene compounds[10]. This is due to the new class of activators or cocatalysts based on boranes which show polymerization activity when used in combination with metallocene for both ethylene and propylene. Details of polymerization studies using metallocene-borane catalyst systems are shown in Table 1.4. Although this catalyst system has low polymerization activity, it is an ideal candidate for mechanistic studies. Even though the major aim in developing these catalyst systems has been to understand the nature of active species, they also provide a hope that a practical catalyst free of MAO and possessing high catalyst activity would be feasible in the near future.

1.3 Synthesis and characterization of methylaluminoxane (MAO)

Aluminoxanes are prepared by controlled hydrolysis of alkylaluminums. The typical structural element is an oxygen atom joining two aluminum atoms that still bear alkyl groups. The simplest representative of aluminoxanes is μ-oxo-bisalkylaluminum or tetraalkyl-dialuminumoxide. Tetraalkyl aluminoxanes were found to be one of the key compounds for the stereospecific polymerization of epoxides and acetaldehyde[43,44,45]. Aluminoxanes have received considerable

Table 1.4 Polymerization Features using Cationic Metallocene Based Single Component Catalysts

Catalyst	Cocatalyst	Polymerization conditions	Activity (Kg-PE/mol-Zr.h)	Reference
$Cp_2Zr(CH_3)_2$	$B(C_6F_5)_3$	Pressure = 1 kg/cm^2, Temperature = 25°C, Time = 40-150 sec	450	41b
$(Cp^*)_2Zr(CH_3)_2$	$[Bu_3NH][B(C_6H_4R)_4]$	Pressure = 6 kg/cm^2, Temperature = 80°C,	375	39a
$(Cp^*)_2Zr(CH_3)_2$	$C_2B_9H_{13}$	Pressure = 16.3 kg/cm^2, Temperature = 40°C,	265	39a
$Cp_2ZrMe(THF)^+$	$^-B(Ph)_4$	Pressure = 1-4 kg/cm^2, Temperature = 25°C,	12	42

attention because of implications for olefin polymerization in Ziegler-Natta catalysis[23,27,30,46,47]. The preferred aluminoxanes for olefin polymerization catalysts contain about 4 to 30 of the repeating units: [-O-AlR-]. where R = CH_3. In the last 10-15 years, considerable research has been done on the synthesis and structural characterization of aluminoxanes used in α-olefin polymerization, copolymerization, stereospecific polymerization of propylene using chiral metallocenes and syndiotactic polymerization of styrene[46-50]. Recent literature generated from patents on aluminoxane synthesis and its use in polymerization of ethylene are summarized in Table 1.5. Any hydrocarbyl aluminum compound on controlled reaction with water forms an aluminoxane. The most commonly used alkylaluminums for the synthesis of aluminoxanes are triisobutylaluminum (TIBAL), triethylaluminum (TEAL) and trimethylaluminum (TMA). Of the various aluminoxanes, MAO is the most difficult to prepare because of the extreme reactivity of TMA. The most reactive MAO is the most preferred one for olefin polymerization.

1.3.1 Synthesis of MAO

Reaction between water and alkylaluminums is highly exothermic, accompanied by flames and yields aluminum oxide. The reaction is carried out in an inert solvent. The preferred solvents are aromatic solvents and the most preferred is toluene. For the careful, controlled and partial hydrolysis of alkylaluminum, several methods have been developed. The methods differ in the carrier that is used to dilute the water to slow down reaction rate. Different methods for synthesis of aluminoxanes depending on the source of water used can be classified in the following way.

1.3.1.1. Direct hydrolysis
1.3.1.2. Crystal water method
1.3.1.3. Other methods of preparation

Table 1.5 Synthesis of Methylaluminoxane (Patent Literature)

Patent No.	C.A. No.	Name of Company	Synthetic parameters	Features
JP 62,148,491	108: 6621y	Mitsui Petro Chemical Ind., Ltd.	$Al(CH_3)_3$ (0.05 mol), $MgCl_2.6H_2O$, Water:$Al(CH_3)_3$ = 1.8, toluene, at 0^0C addition and at 70^0C stirring for 96 h	1.5 g solid MAO, Mol. Wt. 1860, d.p. = 30
PCT Int. Appl. WO 8902434	111: 78885x	BASF A.-G.	$Al(CH_3)_3$ (0.4 mol), Ice, Water:$AlCH_3)_3$ = 0.53, toluene(360 mL), at -80^0C addition and brought to room temperature while stirring	16-17 g solid MAO, soluble in benzene, cumulene, toluene,
EP 315,234	111: 115934k	Texas Alkyls, Inc.	$Al(CH_3)_3$ (chilled), $Al(OH)_3$ was combined with water forming a fluppy solid was used as water source, chilled toluene, 8 h at chilled temperature and overnight at 26^0C	-

Contd....

Table 1.5 Contd....

Patent No.	C.A. No.	Name of Company	Synthetic parameters	Features
JP 01,210,404	112: 78216a	Mitsui Toatsu Chemicals, Inc.	$Al(CH_3)_3$ (0.42 mol), $CuSO_4.5H_2O$, water:$Al(CH_3)_3$= 1.2, toluene(400 mL), at -5^{0}C for 24 h and at 25^{0}C for 24 h	15 g solid MAO
EP 348,126	112:199342x	Exxon Chemical Patents Inc.	$Al(CH_3)_3$ (0.033 mol), triethylboraxine as water source, triethylboraxine:$Al(CH_3)_3$ = 0.33, toluene(50 mL)	MAO solution
EP 383,255	114: 24783f	Idemitsu Kosan Co., Ltd.	$Al(CH_3)_3$ (0.5 mol), $CuSO_4.5H_2O$, water:$Al(CH_3)_3$ = 1.9, ethylbenzene(352 mL), at 0^{0}C addition and 40^{0}C for 9 h	solution was used as MAO, Al content = 1.6 mol. Al/Lit
EP 393,358	114: 43755q	Idemitsu Kosan Co., Ltd.	$Al(CH_3)_3$ (0.25 mol), $CuSO_4$. $5H_2O$, water:$Al(CH_3)_3$ = 1.9, Toluene(200 mL) 40^{0}C, 30 h	7.04 g solid MAO, Mol. Wt. 1100, Toluene soluble

Contd....

Table 1.5 Contd....

Patent No.	C.A. No.	Name of Company	Synthetic parameters	Features
JP 03,74,415	115: 280787e	Asahi Chemical Ind.	$Al(CH_3)_3$(0.52 mol), $CuSO_4.5H_2O$, water:$Al(CH_3)_3$ = 1.44, toluene, 20^0C, 24 h	Mol. Wt. = 640
US 5,099,050	116: 236342c	Ethyl Corp.	$Al(CH_3)_3$, $LiBr.2H_2O$, toluene, at room temperature and at 38^0C	2.5 g Al content
JP 04,49,293	117: 8699q	Idemitsu Kosan K.K.	$Al(CH_3)_3$ (0.13 mol), $CuSO_4.5H_2O$, water:$Al(CH_3)_3$ = 5.26, toluene, at 5^0C addition and at 40^0C reaction done, toluene removed and heated to 110^0C.	4.7 g solid MAO, gelation stopped by solubilizing in 20 mL toluene + 0.9 mL Ortho dichloro benzene
EP 513,808	118: 169789e	Phillips Petroleum Co.	$Al(CH_3)_3$, $FeSO_4.7H_2O$	-

1.3.1.1 Direct hydrolysis

In this method water is used directly with some carrier like inert gas, solvents etc., Depending on the carrier used direct method can be further classified as follows

a) Reaction of alkylaluminums and water in solvents

This is one of the first methods employed for the preparation of aluminoxanes. Water is dispersed in solvents like benzene and then alkylaluminum is added to the benzene containing water to give the aluminoxane[51].

b) Inert gas as water carrier

Nitrogen stream as carrier for water vapor is used in the reaction of alkylaluminums with water to give aluminoxane[52].

c) Condensation method

In this method water vapor is condensed into a cooled solution of alkylaluminum in a solvent like benzene[49].

d) Molecular sieve method

Water adsorbed on a molecular sieve serves as a water source for the synthesis of aluminoxanes[54].

e) Ice method

In this method instead of water, ice is taken in toluene and reacted with alkylaluminum at low temperature[55].

Direct methods are quite hazardous as a runaway reaction can occur very easily. Due to weak physical bonds between water and the carrier, the water is given off quite readily so that controlled reaction conditions are difficult to achieve.

1.3.1.2 Crystal water method

The water needed for partial hydrolysis can also be introduced into the reactor in a chemically bonded form as salt hydrates. In this case the crystal water is given off more slowly so that a controlled reaction is guaranteed. The hydrated salts generally used in the synthesis of aluminoxanes are $CuSO_4.5H_2O$, $FeSO_4.7H_2O$, $Al_2(SO_4)_3.18H_2O$, $Al_2(SO_4)_3.15H_2O$, $Ti(SO_4)_2.8H_2O$, $LiBr.2H_2O$, $LiI.2H_2O$ and so on.

There are few reports for the synthesis of MAO by using different hydrated salts. The types of hydrated salts used, solvent, temperature and other reaction conditions employed for the synthesis of MAO are given in Table 1.6.

The commonly employed solvents are aromatic solvents amongst which toluene is the most preferred. The concentration of TMA compound in the inert solvent is reported to range from 5-20 weight percent by different researchers. The mole ratio of TMA to water in hydrated salt varied between 4:3 to 1:3.5. Temperatures used for the synthesis of methylaluminoxane by this technique are in the range of -78°C to 80°C. The yield reported vary from 35 to 45%. As this process is most widely used for synthesis of MAO, a typical procedure as reported by Gianetti[59] *et al.* is described below.

In this method $CuSO_4.5H_2O$ was used as the source of water. In a 2 L round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a dropping funnel were placed 55 g of fine pulverized $CuSO_4.5H_2O$ and 200 mL of toluene. Five hundred and ten milliliters of a 1.438 mol L^{-1} toluene solution of $Al(CH_3)_3$ were added dropwise at -20°C. After 24 h the reaction temperature was slowly raised to 20°C. (Caution: warming of the slurry to room temperature must be very slow and under controlled conditions. Explosive decomposition may take place!) After filtration a clear toluene solution was obtained. The solution was concentrated under reduced pressure. A solid caramel like residue was obtained. A 1:1 toluene/n-hexane mixture was then

Table 1.6 Synthesis of Methylaluminoxane (Published Literature)

Parameters	Ref. 59	Ref. 66	Ref. 82
$Al(CH_3)_3$	1.032 mol	0.64 mol	0.74 mol
H_2O source	$CuSO_4.5H_2O$	$Al_2(SO_4)_3.18H_2O$	$Al_2(SO_4)_3.15H_2O$
$H_2O:Al(CH_3)_3$	1.102 : 1.03	1.2 : 0.64	1.3 : 0.75
Solvent	toluene(1.5 Lit)	toluene(0.25 Lit)	toluene(0.35 Lit)
Temperature	-20^0C	70^0C	0 and 40^0C
Time	24 h	till 28 Lit CH_4 evolved	several h
% Hydrolysis	-	65%	-
Conversion	24%	35%	35%
Solubility	toluene	up to 75% in C_6H_6	-
Al content	43 - 45%	-	-
CH_4/Al	1.1	-	-
Mol. Wt.	1350-1650(cryoscopy)	250-1400(GPC)	-

Contd....

Table 1.6 Contd....

Parameters	Ref. 54	Ref. 61a	K. Soga[a] et al.,
$Al(CH_3)_3$	0.4 mol	0.52 mol	1.4 mol
H_2O source	Ice block	$FeSO_4.7H_2O$	$Ti(SO_4)_2.8H_2O$
$H_2O:Al(CH_3)_3$	1 : 2	0.60 : 0.52	2.1 : 1.4
Solvent	toluene(0.36 Lit)	toluene(0.15 Lit)	toluene
Temperature	-80^{0}C and room temp.	-10 and 80^{0}C	-20^{0}C and room temp.
Time	till 10 Lit CH_4 evolved	10 min and 3 h (till 22.4 Lit CH_4 evolved)	20 h and 96 h
Hydrolysis (%)	37.2	64	-
Conversion (%)	56	53	-
Solubility	toluene	toluene	-
Al content	44%	-	-
CH_4/Al	1.59	-	1.56 (after treat. with Al_2O_3 for 24 h)
Mol. Wt.	1129(cryoscopy)	900(cryoscopy)	-

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[a] K. Soga, C-H. Yu, T. Shiono, *Makromol. Chem., Rapid Commun.*, **9**, 141, (1988)

added. This process was repeated several times to ensure complete removal of distillative $Al(CH_3)_3$. On drying at 40°C and 1×10^{-6} mm Hg, 12.6 g of a white apparently crystalline solid was obtained.

The MAO synthesized using $CuSO_4.5H_2O$ as water source always contain soluble Cu(I) alkyl compounds complexed with trimethylaluminum[59]. This can be avoided by using aluminum sulfate crystal water. A recent improvement to the crystal water method made by Kaminsky *et al.* is use of partially dehydrated aluminum sulfate as a water source[55]. However, the dehydration process is very uneconomic and insoluble aluminoxanes produced during the hydrolysis cannot be separated from the residual aluminum sulfate. A complete mass balance of the reaction is nearly impossible. Recently a process for the synthesis of MAO using $LiBr.2H_2O$ as water source has been reported which leads to a more soluble MAO[56a]. MAO also undergoes gelation upon storage. It has been reported that addition of small quantities of dodecanol or tri-n-octylamine (3 wt%) delays the onset of gelation[56b].

1.3.1.3 Other methods of preparation

Efforts at producing the Al-O-Al group with appropriately chosen organoaluminum compounds like dialkylaluminum chloride and lithiumdialkylaluminate have been made[48,58]. The reactions between alkoxy aluminum dichlorides and methylaluminum dichloride or between methoxyaluminum compounds ($Me_x(OMe)AlCl_{2-x}$; x = 0,1,2) and methylaluminum compounds (Me_yAlCl_{3-y}; y = 1,2,3) in the presence of TEAL have also been shown to yield aluminoxanes[50c,58]. Another way to prepare aluminoxanes is the reaction of PbO with aluminum trialkyls[59].

1.3.2 Properties of MAO

The isolated aluminoxanes obtained as residues of solvent distillation are white amorphous powders or glassy material soluble in toluene but insoluble in n-hexane. The amorphous nature of MAO has been confirmed by X-ray powder diffraction technique. The degree of oligomerization generally varies from 5-30 and the molecular weight range is 250-1700 as determined cryoscopically using benzene as solvent. Methyl/Al ratio varies from 1.1 to 1.6 as reported by different authors. Al content varies from 43 to 45%. MAO always contains some amount of TMA which cannot be removed easily by vacuum distillation.

1.3.3 Characterization of MAO

1.3.3.1 Infrared spectroscopy

The IR spectrum of $[\text{-O-Al(CH}_3\text{)-}]_n$ shows a very intense absorption region around 800 cm^{-1} attributable to Al-O-Al stretching vibrations[59].

1.3.3.2 ^{1}H-NMR[59-61]

The ^{1}H-NMR spectrum displays a broad band centered at -0.35 ppm, attributable to the methyl protons of the oligomeric $[\text{-O-Al(CH}_3\text{)-}]_n$. The methyl resonance band is intermediate to that of the protons in the TMA methyl group (-0.20 ppm) and the band reported for $[(CH_3)_2Al]_2O$[48]. The observed broadening of the resonance line may be attributed either to the presence of the species having different structures (cyclic or linear) or to the polymeric nature and tendency of the MAO to associate in the form of aggregates. The ^{1}H-NMR spectrum of MAO is shown in Figure 1.4.

1.3.3.3 ^{13}C-NMR

The ^{13}C-NMR spectrum[59] shows an intense, broad band at -6.55 ppm. The reported spectrum of $Al(CH_3)_3$ at room temperature consists of a single sharp resonance at -7.28 ppm. For all the other methylalkoxy aluminum compounds the methyl resonance is observed to be extremely broad apparently due to quadrupolar coupling of the methyl carbon with the ^{27}Al nucleus ($I = 5/2$)[63]. The down field shift of the observed resonance is in accordance with the inductive effect of the oxygen atoms. Further structural information are, however, not accessible owing to the quadrupolar relaxation by ^{27}Al. The ^{13}C-NMR spectrum of MAO is shown in Figure 1.5.

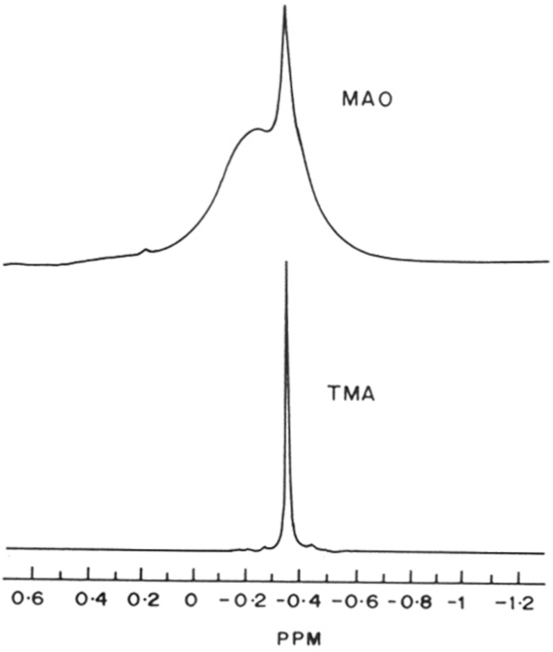


Fig. 1.4 ^{1}H-NMR spectrum of TMA and MAO in toluene-d_8

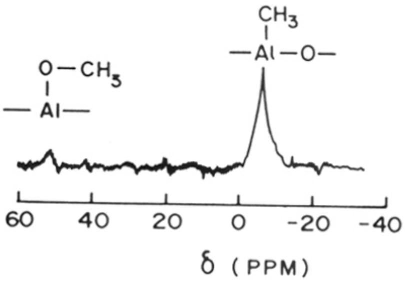


Fig. 1.5 ^{13}C-NMR spectrum of MAO in benzene-d_6

1.3.3.4 ^{27}Al-NMR

Nekhaeva et al[64]., showed that MAO has two peaks, at approximately 150 and 70 ppm, but later Sugano et al[65]., and Mason et al[69]., independently reported that for MAO only one peak exists at approximately 154 ppm and this value is nearly the same for TMA except the line width which is wider for MAO. MAO line width is 1400 Hz whereas TMA line width is 950 Hz. They have reported the plausible structure of MAO as a tetracoordinated one. The line width is related to the mobility of the Al atom. MAO is liable to move in toluene solution. The narrower line width at high temperature indicates a capability to move more freely at high temperature and also chemical shift at lower field, indicates a slightly weak tetracoordinated structure. The ^{27}Al-NMR spectrum of MAO is shown in Figure 1.6.

1.3.3.5 U.V.

The 250-350 nm region of the UV spectrum of benzene solution of the MAO is reproduced[59] in Figure 1.7. A broad band appears at 286 nm (ε_{max} = 10^{-} Lit. mol^{-1}). In the near UV region only the non bonding electrons of bridging oxygens are available for an electronic transition. Analogous saturated organic compounds, such as polyethers, absorb, however, at considerably shorter wavelength. This bathochromic shift may be explained on the grounds of a strong interaction on the nonbonding oxygen electrons with neighboring aluminum atoms. For oxygen bridged organoaluminum compounds there is considerable supporting evidence for the existence of an oxygen to aluminum Pπ-dπ dative bond. A delocalized structure, as shown below, can be, therefore, inferred for the oligomeric MAO.

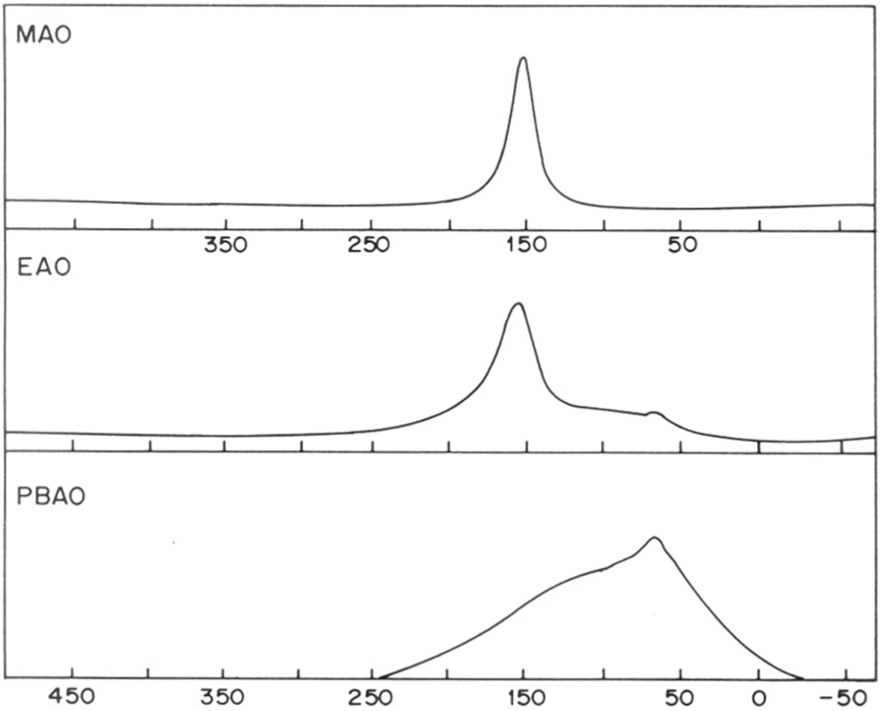


Fig. 1.6 ^{27}Al-NMR spectrum of aluminoxanes

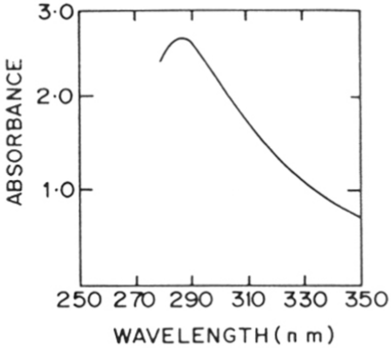


Fig. 1.7 U.V. absorption spectrum of MAO in benzene at room temperature. Solvent spectrum subtracted

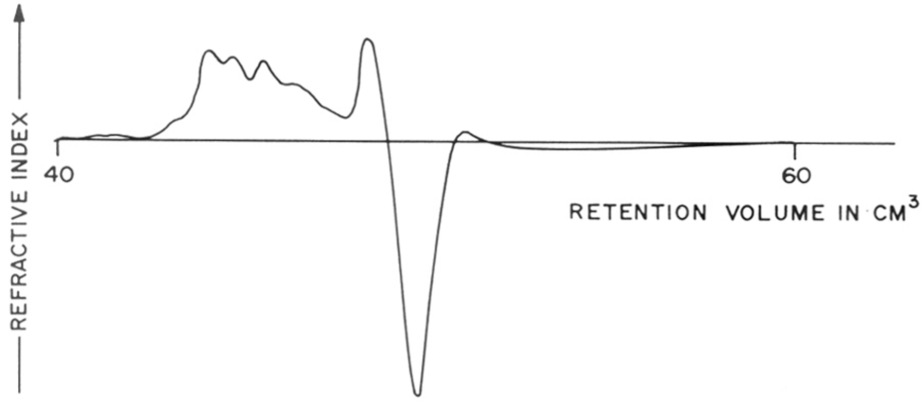


Fig. 1.8 Gel Permeation Chromatogram of MAO

1.3.3.6 Mass spectrometry

Kaminsky reported[28] a mass spectrum of synthesized MAO which was recorded after successfully isolating a fraction of MAO by fractional precipitation. The isolated MAO shows a M+ peak at 290 which was attributed to a cyclic MAO structure containing 5 Al atoms.

Later Giannetti et al[59]., reported that the mass spectra of the powders of MAO showed peaks at m/e values higher than 300 attributable to ion fragments containing both aluminum and methyl groups. However, they were not able, as already reported by Kaminsky, to assign these peaks to any cyclic oligomeric structure.

1.3.3.7 Gel Permeation chromatography

Characterization of MAO by GPC reveals the presence of different oligomeric products. Using a suitable series of columns and alkyl aluminum compounds with known molecular weight, it is possible to obtain the average molecular weights of most species which are present in MAO. Cam and Albizatti[66] reported that MAO is a complex mixture containing, besides TMA, many compounds with molecular weights between 250 and 1500 (Figure 1.8). The composition of the mixture is related to the conditions employed during the separation of the product.

1.3.3.8 X-Ray crystallography

The coordination number of aluminum in methylaluminoxane can be determined by x-ray crystallography. The first crystallographic evidence for aluminum to have coordination number of four in aluminoxane was provided by Atwood and Zaworotko with their structural determination of the $[Al_7O_6Me_{16}]^-$ anion[68] (Figure 1.9c). Recently Mason[69] *et al.* have shown for the first time that alkylaluminoxanes like their hydroxy siloxy companions, have a 3-dimensional structure, comparable, not to a dense mineral structure but to the open cage structure of the well-characterized iminoalanes $[RAlNR']_n$ (Figure 1.9e). Based on the x-ray crystallographic studies on tert-butyl aluminoxane Mason *et al.* have stated that aluminum in alkylaluminoxanes is tetracoordinated, in agreement with the earlier studies[69].

1.3.4 Structure of MAO

MAO is an oligomer with a degree of oligomerization varying between 5-28. The repeat unit is -[Al(CH_3)-O-]-. Based on different studies various researchers have proposed different structures for MAO. On the basis of the known structure of dialkylsiloxane polymers, alkylaluminoxanes were originally proposed to have a linear chain structure consisting of alternate aluminum and oxygen atoms[67]. Based on mass spectroscopy, Kaminsky reported[28] the structure of MAO as cyclic (Figure 1.9a). Such structures would obviously require the aluminum to have a coordination number of three, which is rare, only existing in compounds in which oligomerization is hindered by sterically bulky ligands. Since it is common for aluminum to maximize its coordination number through the formation of dimers and trimers through bridging ligands, the majority of workers have since proposed that the aluminum has a coordination number of four[67]. Giannetti[59] *et al.* and Sugano[65] *et al.* have independently proposed the structure of MAO as linear-tetracoordinated (Figure 1.9b). The first crystallographic evidence for aluminum to have coordination number of four in aluminoxane was provided by Atwood and Zaworotko with their structural determination of the $[Al_7O_6Me_{16}]^-$ anion[68] (Figure 1.9c). The similarity of this structure to those of dimeric and trimeric alkoxide compounds of aluminum has prompted many groups to propose structures based on either four- or six-membered rings or both[67] (example Figure 1.9d). Although these models do appear to be reasonable since they more closely follow known aluminum chemistry, significant problems remain, namely, that while the core aluminum centers are coordinatively saturated, the periphery remains three coordinate. Recently Mason[69] *et al.* have shown that alkyl aluminoxanes like their

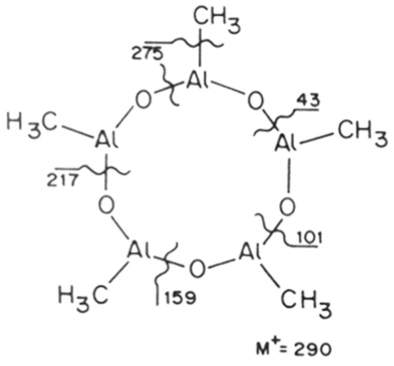


Fig. 1.9a Cyclic structure of MAO

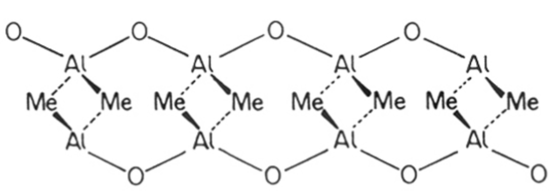


Fig. 1.9b Linear tetra coordinated structure of MAO

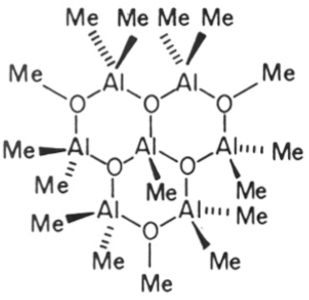


Fig. 1.9c Structure of the $[Al_7O_6Me_{10}]^-$ anion

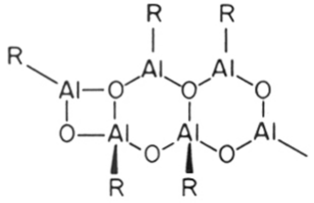


Fig. 1.9d Fused four and six membered ring structure

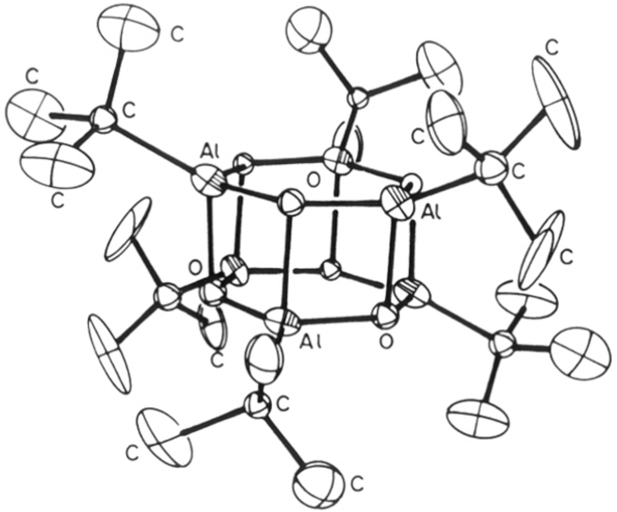
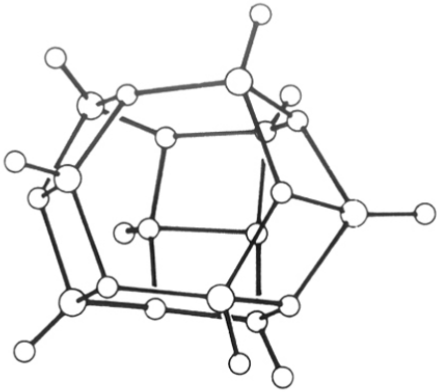
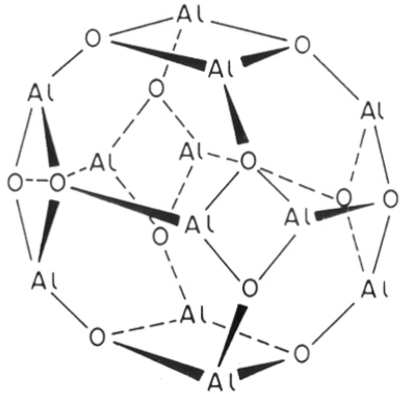


Fig. 1.9e (1) Molecular structure of tert-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_6$. All the hydrogen atoms are omitted for clarity



(2) Molecular structure of tert-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_9$. Methyl groups are omitted for clarity



(3) Plausible molecular structure of tert-butylaluminoxane $[(^tBu)Al(\mu_3\text{-}O)]_{12}$. ^{t}Butyl groups are omitted for clarity

hydroxy siloxy companions, have a 3-dimensional structure, comparable, not to a dense mineral structure, but to the open cage structure of the well-characterized iminoalanes $[RAlNR']_n$ (Figure 1.9e).

1.3.5 Role of free alkylaluminum in MAO

Despite its uniqueness as cocatalyst, MAO still remains a "black box" whose structure is postulated as being an oligomeric (cyclic or linear) chain of $-[Al(CH_3)-O-]-$ units. Depending on the nature of the hydrated salt used for synthesis and reaction conditions, MAO with widely differing activities as cocatalysts in polymerization of ethylene is formed. Sinn and coworkers proposed that MAO forms an adduct with three molecules of TMA which even after distillation in the presence of cumene or complexation with tetrahydrofuran retained one molecule of strongly associated TMA[54]. The presence of residual TMA in MAO can also be detected by GPC[66] and by ^{1}H-NMR. In fact, it has been speculated that TMA might be the actual cocatalyst in MAO based catalyst systems[61a]. The proton spectrum of a MAO sample in toluene-d_8 shows two main resonances, one very broad at -0.21 ppm and another one slightly broad at -0.36ppm. When a solid MAO sample is heated in vacuo for several hours at 100-120^{0}C, the resonance at -0.36 ppm decreases in intensity, as TMA is liberated. By comparison with authentic sample this peak was assigned to free TMA (as the trimer of Al_2Me_6). This assignment was confirmed by low temperature NMR[61b]. Resconi *et al.* based on these observations speculated that the equilibrium shown in Equation 1.2 must occur in toluene solution.

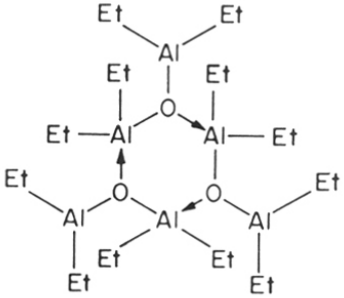
$$\text{MAO.nTMA} \quad = \quad \text{MAO.(n-m)TMA} + \text{(m/2)(TMA)} \qquad (1.2)$$

Even if the peaks of MAO and TMA are partially overlapped, the molar ratio of the two compounds can be evaluated. Thus, the amount of free TMA in toluene in the spectrum reported by Resconi *et al.* is 3.5%[61a]. The slight broadening of the line at -0.36 ppm could be due to the reversible adduct formation between MAO and TMA in solution (coalescence of the two peaks is observed at 90°C). It is reported that TMA present along with MAO acts as a chain transfer agent when $Cp_2Zr(CH_2C_6H_5)_2$ is used as catalyst for the polymerization of ethylene[59].

1.3.6 Synthesis and characterization of aluminoxanes derived from other alkylaluminums[48-50]

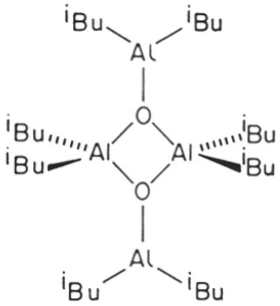
Apart from MAO, most commonly used aluminoxanes are ethylaluminoxane and isobutylaluminoxane which are synthesized by the partial hydrolysis of TEAL and TIBAL respectively. Of the cocatalysts, MAO is much more effective than ethylaluminoxane or isobutylaluminoxane.

When TEAL in benzene reacts with water in the ratios of 2:1 and 1:1 the products are tetraethyldialuminoxane $(Et_2Al)_2O$ and EtAlO respectively. $(Et_2Al)_2O$ is a viscous liquid and is thermally stable at room temperature but, on attempted distillation under reduced pressure above 100^0C, it decomposes to yield a volatile, colorless, mobile liquid and a nonvolatile, slightly tacky, white solid. Strong absorption bands around 800 cm^{-1} characteristic of Al-O-Al linkages are observed for $(Et_2Al)_2O$. From the molecular weight data (cryoscopy) it has been found to be a trimer bearing the structure



EtAlO compound is found to be oligomeric in nature.

Tetraisobutylaluminoxane has been prepared by the reaction of 2 moles of TIBAL with 1 mole of water in toluene. IR spectrum shows the characteristic band of Al-O-Al linkage around 800 cm^{-1} and from cryoscopic molecular weight data and NMR the compound iBu_4Al_2O has been found to be dimeric in nature. The structure of the compound is



The nature of reaction products of TEAL with water at a molar ratio of 2 : 1 has been recently studied by Siergieczyk and Synoradzki[70]. By GPC studies it has been found that raw tetradialuminoxane consists of ethyloligoaluminoxanes, a tetrahydrodialuminoxane trimer and TEAL.

1 : 1 reaction product of TEAL and water has been found to be oligomeric in nature which is in dynamic equilibrium (Equation 1.3)[71]

$R_2Al(OAlR)_{n-1}OAlR_2.(n-1)R_3Al == R_2Al(OAlR)_{n-1}OAlR_2 + 1/2(n-1)(R_3Al)_2$ (1.3)
where R = TEAL

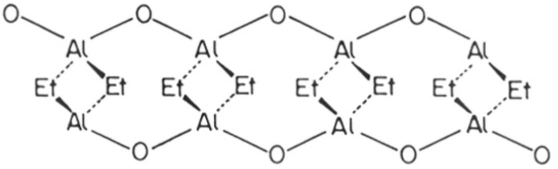
Several aluminoxanes have been characterized by ^{27}Al-NMR by Sugano et al[66]., (Figure 1.6). The chemical shift of ethylaluminoxane is approximately 152 ppm and the line width 2320 Hz. The plausible structure of the ethylaluminoxane has been reported as a tetracoordinated structure and relatively free to move in toluene solution. The chemical shifts and line widths of isobutylaluminoxane are 66 ppm/570 Hz and 78 ppm/9960 Hz. So, aluminum in isobutylaluminoxane has a different coordination structure as compared to ethylaluminoxane and MAO. The plausible structures of ethylaluminoxane and isobutylaluminoxane proposed by Sugano et. al., are shown in Figure 1.10.

1.4 Group IVA metallocene-MAO catalyst system for ethylene polymerization

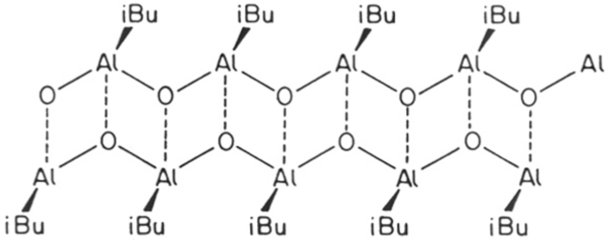
Titanocene when activated by organoaluminum halides was first shown by Breslow and Newburg to function as a homogeneous olefin polymerization catalyst[14]. A bimetallic complex having tetravalent titanium was believed to be the active species. The catalyst underwent rapid deactivation by bimolecular reductive disproportionation[16]. The inactive trivalent titanium species could be reactivated by oxidation with oxygen. Sinn, Kaminsky and coworkers subsequently investigated zirconocene dichloride for ethylene polymerization[28,72]. These titanium and zirconium catalyst systems exhibit only modest activity in the case of poly(ethylene), produce polymer of relatively low molecular weight and do not polymerize higher olefins. A major advance in the application of group 4 metallocene type catalysts for Ziegler-Natta polymerizations occurred when Kaminsky and coworkers discovered that a combination of either Cp_2MCl_2 (M = Ti, Zr) or halide-free $Cp_2M(CH_3)_2$ systems and oligomeric MAO (formed from TMA and a source of water) were exceedingly active catalysts, and rapidly polymerized ethylene as well as propylene[28]. Later workers, namely, Natta, Chien, Giannini, Gianetti, Resconi and others have substantially contributed to the understanding of ethylene polymerization using homogeneous Ziegler-Natta catalyst systems.

The ethylene polymerization features reported by various researchers using Group IVA metallocene-MAO catalyst systems are discussed in detail in the following sections.

1.4.1. Effect of transition metal
1.4.2. Effect of ligands around the transition metal
1.4.3. Effect of cocatalyst(Al)/catalyst (metal) ratio



ETHYLALUMINOXANE



ISOBUTYLALUMINOXANE

Fig. 1.10 Plausible structures of ethylaluminoxane and isobutyl aluminoxane

1.4.4. Effect of temperature
1.4.5. Effect of time
1.4.6. Effect of hydrogen
1.4.7. Effect of the nature of alkyl group in aluminoxane
1.4.8. Effect of molecular weight of MAO
1.4.9. Effect of TMA in MAO on the polymerization of ethylene
1.4.10. Kinetics and mechanism of polymerization
1.4.11. Supported metallocene catalysts
1.4.12. Representative patent literature

1.4.1 Effect of transition metal

Ti, Zr and Hf are the most commonly used transition metals for the polymerization of ethylene. Metallocenes based on different Group IVA transition metals have varying activity for ethylene polymerization. Literature data showing the effect of transition metal on ethylene polymerization is summarized in Table 1.7.

Kaminsky *et al.* have stated that for ethylene polymerizations employing $Cp_2M(CH_3)_2$/MAO (M = Ti, Zr, Hf), the zirconium catalyst is more active than the titanium or hafnium catalysts, especially at temperatures over 50°C[73]. Gianetti *et al.* also reported highest catalyst activities with Zr-based systems[59]. Considerably lower activities were achieved by the hafnium metallocenes. Ethylene polymerizations were studied by Chien[76] *et al.* using Cp_2ZrCl_2/MAO and Cp_2HfCl_2/MAO at 1.7 atm of ethylene pressure. The Hf catalysts showed about two thirds the activity of the Zr catalyst. This difference may be attributed to the greater number of active centers present in the Zr catalyst ($C^* = 52\%$ for Cp_2HfCl_2 and $C^* = 80\%$ for Cp_2ZrCl_2)

The activity of the Cp_2ZrCl_2/MAO catalyst has been found to be inversely proportional to the Zr concentration. This was interpreted as due to a decrease of bimolecular deactivation. In contrast, variation of activity with Hf concentration is less pronounced[76].

Table 1.7 Effect of Transition Metal on Ethylene Polymerization using Metallocene/MAO Catalyst System

Catalyst system	Polymerization conditions	Activity (Kg-PE/g-met.h.atm)	Features	Reference
Cp_2TiCl_2	$[Ti] = 3 \times 10^{-6}$ M, 20°C	90	$\bar{M}v = 4.3 \times 10^5$	89
Cp_2ZrCl_2	$[Zr] = 4.8 \times 10^{-6}$ M, Al/Zr = 11700, 70°C, 1.7 atm	154	$\bar{M}v = 0.27 \times 10^5$	74
Cp_2HfCl_2	$[Hf] = 4.8 \times 10^{-6}$ M, Al/Hf = 11700, 70°C, 1.7 atm	42	$\bar{M}v = 0.45 \times 10^5$	74
$Cp_2Ti(CH_3)_2$	$[Ti] = 3 \times 10^{-6}$ M, 20°C,	5	$\bar{M}v = 5.2 \times 10^5$	89
$Cp_2Zr(CH_3)_2$	$[Zr] = 3 \times 10^{-7}$ M, Al/Zr = 14000, 50°C, 3 atm	107	$\bar{M}v = 3.31 \times 10^5$, MWD = 1.8	59
$Cp_2Hf(CH_3)_2$	$[Hf] = 3 \times 10^{-7}$ M, Al/Hf = 15000, 50°C, 3 atm	18	$\bar{M}v = 3.6 \times 10^5$	59
$Cp_2Ti(C_6H_5)_2$	$[Ti] = 3 \times 10^{-7}$ M, Al/Ti = 17000, 50°C, 3 atm	63	$\bar{M}v = 5.7 \times 10^5$, MWD = 1.73	59
$Cp_2Zr(C_6H_5)_2$	$[Zr] = 3 \times 10^{-7}$ M, Al/Zr = 18000, 50°C, 3 atm	328	$\bar{M}v = 2.9 \times 10^5$	59
$Cp_2Hf(C_6H_5)_2$	$[Hf] = 3 \times 10^{-7}$ M, Al/Hf = 12000, 50°C, 3 atm	32	$\bar{M}v = 3.8 \times 10^5$	59

The Hf catalyst shows a smaller dependence of polymer molecular weight on temperature. Depending upon the polymerization conditions (concentration of transition metal and MAO and temperature) the polymer obtained with the Hf catalyst can have higher molecular weight (>50°C) or lower molecular weight (<50°C) than the polymer obtained with the Zr catalyst. Titanium based catalysts are more active at lower temperature. These catalysts show low polymerization activity as compared to Zr and high polymerization activity as compared to Hf based catalysts. Due to these reasons Zr based metallocenes have assumed generally greater importance.

1.4.2 Effect of ligands around the transition metal

The data available in literature on the effect of ligands around the transition metal for polymerization of ethylene is summarized in Table 1.8. Bis(cyclopentadienyl) titanium(IV) and bis(cyclopentadienyl) zirconium(IV)- compounds together with MAO have shown to be the most useful homogeneous Ziegler-Natta catalysts for ethylene polymerization. Ring substituted zirconocenedichlorides, especially bis(pentamethylcyclopentadienyl) zirconiumdichloride $(CpMe_5)_2ZrCl_2$, have been used as catalyst for polymerization of ethylene. $(CpMe_5)_2ZrCl_2$ shows a lower activity (by a factor of 5 to 10) compared to bis(cyclopentadienyl) zirconiumdichloride. However, the molecular weight of the poly(ethylene)s produced by the former was twice that of the latter. With $(CpMe_5)_2ZrCl_2$ the highest reported molecular weight of 1,500,000 ($\bar{M}\eta$) has been achieved. However the polydispersity was between 6 and 15 which is much broader than that obtained with Cp_2ZrCl_2. This has been attributed to the presence of two active centers with widely varying reaction rates as well as ability for monomer insertion.

Gianetti *et al.* achieved high catalyst activities with the $Cp_2Zr(C_6H_5)_2$, $Cp_2Zr(CH_2C_6H_5)_2$ and $Cp_2Zr[-CH_2Si(CH_3)_3]_2$ complexes. A remarkably high activity, compared with $Cp_2Zr(CH_3)_2$, was achieved by related π-indenyl complex $(Ind)_2Zr(CH_3)_2$. When bis(π-fluorenyl) analog was employed as catalyst component,

Table 1.8 Effect of Ligands Around the Transition Metal for Ethylene Polymerization using Metallocene/MAO Catalyst System

Catalyst system	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Features	Reference
Cp_2ZrCl_2	[Zr] = 1 x 10^{-6} M, Al/Zr = 15000, 70°C, 6-8 atm	323	$\bar{M}v = 1.2 \times 10^5$	73
$Cp(CpMe_5)ZrCl_2$	[Zr] = 1 x 10^{-6} M, Al/Zr = 15000, 70°C, 6-8 atm	63	$\bar{M}v = 7.7 \times 10^5$	73
$(CpMe_5)_2ZrCl_2$	[Zr] = 1 x 10^{-6} M, Al/Zr = 15000, 70°C, 6-8 atm	42	$\bar{M}v = 2.7 \times 10^5$, MWD = 6-15	73
$Cp_2Zr(CH_3)_2$	[Zr] = 3 x 10^{-7} M, Al/Zr = 14000, 50°C, 3 atm	107	$\bar{M}v = 3.31 \times 10^5$, MWD = 1.8	59
$Cp_2Zr(C_6H_5)_2$	[Zr] = 3 x 10^{-7} M, Al/Zr = 18000, 50°C, 3 atm	328	$\bar{M}v = 2.87 \times 10^5$, MWD = 1.7	59
$Cp_2Zr(CH_2C_6H_5)_2$	[Zr] = 3 x 10^{-7} M, Al/Zr = 14500, 50°C, 3 atm	385	$\bar{M}v = 3.25 \times 10^5$, MWD = 1.9	59
$Cp_2Zr(CH_2SiMe_3)_2$	[Zr] = 3 x 10^{-7} M, Al/Zr = 14000, 50°C, 3 atm	567	$\bar{M}v = 3.22 \times 10^5$, MWD = 2.3	59
Ind_2ZrMe_2	[Zr] = 3 x 10^{-7} M, Al/Zr = 22000, 50°C, 3 atm	726	$\bar{M}v = 3.95 \times 10^5$, MWD = 2.2	59
$Zr(CH_2C_6H_5)_4$	[Zr] = 3 x 10^{-7} M, Al/Zr = 15000, 50°C, 3 atm	19	$\bar{M}v = 5.35 \times 10^5$, MWD = 2.2	59
$(\eta^5\text{-}RC_5H_4)_2ZrCl_2$				
R = H	[Zr] = 2.4 x 10^{-5} M, Al/Zr = 1000, 60°C, 1 atm	100	C^* = 0.94 mol/mol.Zr Rp = 9.1 Kg.PE/mmol.Zr.h	75
R = Me	[Zr] = 2.4 x 10^{-5} M, Al/Zr = 1000, 60°C, 1 atm	111	C^* = 0.98 mol/mol.Zr Rp = 10.1 Kg.PE/mmol.Zr.h	75
R = n-Pr	[Zr] = 2.4 x 10^{-5} M, Al/Zr = 1000, 60°C, 1 atm	106	Rp = 9.7 Kg.PE/mmol.Zr.h	75
R = i-Pr	[Zr] = 2.4 x 10^{-5} M, Al/Zr = 1000, 60°C, 1 atm	105	Rp = 9.6 Kg.PE/mmol.Zr.h	75
R = t-But	[Zr] = 2.4 x 10^{-5} M, Al/Zr = 1000, 60°C, 1 atm	83	C^* = 0.99 mol/mol.Zr Rp = 7.6 Kg.PE/mmol.Zr.h	75

only traces of polymer were recovered[59]. It has been proposed that reactive intermediates for soluble Ziegler-Natta catalysts are cationic alkyls[33]. Due to the steric effect or electron donating power of ligands the resulting cationic species may get stabilized or destabilized and result in increase or decrease in catalyst activity. Due to steric effects the fundamental steps involved in the polymerization process, such as alkyl migration or olefin insertion, may be either retarded or accelerated.

The effect of substituents on the cyclopentadienyl rings η^5-$RC_5H_4)_2ZrCl_2$ (where R = H, Me, n-Pr, iPr and t-Bu) was studied in detail by Tait[75] and coworkers. Increase in rate and kp for ethylene polymerization was observed according to the order t-Bu<H<i-Pr<n-Pr<Me. Active center concentration, C^* remained more or less constant for all the catalyst systems.

The inductive and hyper conjugative effects of alkyl substituents will increase the electron density of η^5-cyclopentadienyl ligand leading to the increased electron density at the zirconium atom which in turn leads to an increased rate of polymerization. This increase in polymerization rate may be due to a lowering of the stability of η^2-alkene-zirconium bond resulting in a more weakly coordinated monomer, facilitating insertion into the growing polymer chain. Alternatively, or, in addition, a higher electron density at zirconium atom may weaken the zirconium-carbon σ-bond of the growing polymer chain which could also facilitate insertion of the monomer and hence lead to increased rate of polymerization.

Opposing these effects an increase in the steric bulk of the alkyl substituent may hinder the approach of the incoming monomer and decrease the rate of polymerization. Thus, the observed rates of polymerization and activities may then reflect a combination of the steric and electronic effects and may reach a maximum when R = Me.

1.4.3 Effect of cocatalyst/catalyst (Al/metal) ratio

Effect of Al/metal ratio mainly influences catalyst activity, molecular weight and kinetic profile of polymerization. The effect of Al/metal ratio on ethylene polymerization is summarized in Table 1.9.

Chien and Wang have explored the effect of Al/metal for the polymerization of ethylene using Cp_2ZrCl_2 and $CpZrCl_3$ systems[76]. The effects of [metallocene] and [MAO] were investigated by holding the former constant while varying the latter and vice versa. In the case of Cp_2ZrCl_2/MAO catalyst system, both the shape of polymerization rate profile and activity are only slightly dependent on [MAO] (Table 1.9 and Figure 1.11). A large increase of activity was observed with the decrease of $[Cp_2ZrCl_2]$ (S. No. 1 & 4 of Table 1.9). The activity of $CpZrCl_3$/MAO system is more dependent on [MAO] than in the case of Cp_2ZrCl_2/MAO; a five fold increase of [MAO] raises activity by a factor of two.

It has been reported that the number of active sites $[C^*]$, lies between 75 and 100% of the Zr compounds. Therefore activity should be independent of [Zr][76]. But in reality activity is found to increase with the decrease of catalyst concentration. This is due to the increase of kp(rate constant of propagation). The activity has been found to be proportional to the $[Cp_2ZrCl_2]^{-0.77}$ when log plot of activity versus $[Cp_2ZrCl_2]$ is plotted. This indicates faster propagation at low $[Cp_2ZrCl_2]$. This aspect is further discussed in section 1.4.10.

1.4.4 Effect of temperature

Temperature influences mainly the molecular weight of the polymer as well as the polymerization activity. It is a common characteristic of Ziegler-Natta catalysis that there is an optimum temperature range for maximum activity, below or above which catalyst activity decreases. The variation of catalytic activity and molecular weight with temperature is shown in Table 1.10. When temperature is plotted against catalyst activity there is a broad regime where the activity is relatively constant and it decreases at lower temperatures. The molecular weight of the

Table 1.9 Effect of Al/Metal on Ethylene Polymerization using Metallocene/MAO Catalyst System

Catalyst system	Al/Metal	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Reference
Cp_2ZrCl_2	521	[Zr] = 4.8 x 10^{-5} M, 70°C, 1.4 atm	16.6	76
Cp_2ZrCl_2	1071	[Zr] = 4.8 x 10^{-5} M, 70°C, 1.4 atm	20	76
Cp_2ZrCl_2	2125	[Zr] = 4.8 x 10^{-5} M, 70°C, 1.4 atm	23	76
Cp_2ZrCl_2	22730	[Zr] = 1.1 x 10^{-6} M, 70°C, 1.4 atm	328	76
Cp_2ZrCl_2	46730	[Zr] = 1.1 x 10^{-6} M, 70°C, 1.4 atm	394	76
Cp_2ZrCl_2	92730	[Zr] = 1.1 x 10^{-6} M, 70°C, 1.4 atm	490	76
$CpZrCl_3$	1060	[Zr] = 4.8 x 10^{-6} M, 50°C, 1.4 atm	6.6	76
$CpZrCl_3$	2710	[Zr] = 4.8 x 10^{-6} M, 50°C, 1.4 atm	15.2	76
$CpZrCl_3$	5420	[Zr] = 4.8 x 10^{-6} M, 50°C, 1.4 atm	34.3	76

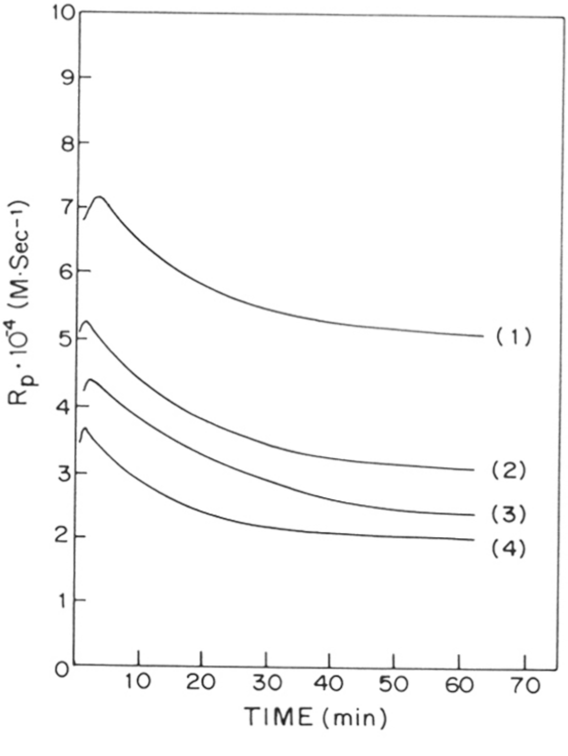


Fig. 1.11 Kinetic profile for the ethylene polymerization catalyzed by Cp_2ZrCl_2-MAO: (1) Al/Zr = 93,400 (2) Al/Zr = 46,700 (3) Al/Zr = 23,500 (4) Al/Zr = 15,200; [Zr] = 1.1×10^{-6} mol/Lit

Table 1.10 Effect of Temperature on Ethylene Polymerization using Metallocene/MAO Catalyst System

Catalyst system	Temp. (°C)	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Features	Reference
Cp_2ZrCl_2	0	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	4.0	$\bar{M}v = 460 \times 10^3$	82
Cp_2ZrCl_2	30	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	17.0	$\bar{M}v = 200 \times 10^3$	82
Cp_2ZrCl_2	50	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	16.0	$\bar{M}v = 65 \times 10^3$	82
Cp_2ZrCl_2	70	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	19.0	$\bar{M}v = 11 \times 10^3$	82
Cp_2ZrCl_2	80	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	16.0	$\bar{M}v = 12 \times 10^3$	82
Cp_2ZrCl_2	90	$[Zr] = 4.75 \times 10^{-5}$ M, Al/Zr = 1070, 1.5 atm	-	$\bar{M}v = 6 \times 10^3$	82
$(CpMe_5)_2ZrCl_2$	20	$[Zr] = 1 \times 10^{-6}$ M, Al/Zr = 15000, 6-8 atm	9.04	$\bar{M}v = >1500$	73
$(CpMe_5)_2ZrCl_2$	70	$[Zr] = 1 \times 10^{-6}$ M, Al/Zr = 15000, 6-8 atm	41.6	$\bar{M}v = 270$	73

polymer decreases monotonically with increasing temperature. The activation energy was found to be 34 KJ/mol for Cp_2ZrCl_2/MAO catalyst system. These results may be attributed to increase of both propagation and deactivation with increasing temperature. Chien and Wang have speculated on the possible mechanism for deactivation[76]. One possibility is a slow dissociation of complexed MAO (Equation 1.4).

$$C^{*}_{i} - P \text{------>} C^{*}_{i-n} - P + n\,\text{MAO} \qquad (1.4)$$

where $C^{*}_{i} = C^{*}$ with "i" number of MAO complexed with it.

The C^{*}_{i-1} is less protected by MAO than C^{*}_{i} and in fact if i-n = 0, rapid bimolecular deactivation occurs. A second possible deactivation mechanism is by β-hydride elimination to give metallocene hydride which has very low propensity for monomer insertion.

At optimum temperature, the catalysts show higher rate of propagation and less of deactivation due to which the high activity is observed. Above the optimum temperature, rates of propagation as well as deactivation increase and below the optimum temperature rates of propagation as well as deactivation decrease and as a net result low activities will be observed. At low temperature the chain transfer rate is low on account of which high molecular weight polymers are produced.

1.4.5 Effect of time

The variation of molecular weight of poly(ethylene)s with polymerization time has been studied for different catalyst systems. With increase in polymerization time and decrease in catalyst concentration the molecular weight is reported to be increased. The literature data is summarized in Table 1.11.

Chien and Wang[76] have studied the variation of poly(ethylene) molecular weight with polymerization time for the catalysts Cp_2ZrCl_2 at [Zr] of 4.8×10^{-5} and 3.8×10^{-6}, and $CpZrCl_3$ catalysts at a [Zr] of 3.8×10^{-6} mol/L. The polymer obtained after 5 min of polymerization had a $\bar{M}n$ 4000 which increases by 43% to a value of 5700

Table 1.11 Effect of Time on Ethylene Polymerization using Metallocene/MAO Catalyst System

Catalyst system	Time (min)	Polymerization conditions	Features	Reference
Cp_2ZrCl_2	5	$[Zr] = 4.8 \times 10^{-5}$ M, Al/Zr = 1070, 70°C, 1.4 atm	$\bar{M}n = 0.04 \times 10^5$, MWD = 3.2	76
Cp_2ZrCl_2	40	$[Zr] = 4.8 \times 10^{-5}$ M, Al/Zr = 1070, 70°C, 1.4 atm	$\bar{M}n = 0.06 \times 10^5$, MWD = 3.1	76
Cp_2ZrCl_2	5	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}n = 0.21 \times 10^5$, MWD = 2.2	76
Cp_2ZrCl_2	20	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}n = 0.18 \times 10^5$, MWD = 2.2	76
Cp_2ZrCl_2	40	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}n = 0.21 \times 10^5$, MWD = 2.1	76
$CpZrCl_3$	5	$[Zr] = 4.8 \times 10^{-5}$ M, Al/Zr = 1070, 70°C, 1.4 atm	$\bar{M}w = 0.3 \times 10^5$, $\bar{M}n = 0.11 \times 10^5$, MWD = 2.7	76
$CpZrCl_3$	10	$[Zr] = 4.8 \times 10^{-5}$ M, Al/Zr = 1070, 70°C, 1.4 atm	$\bar{M}w = 0.26 \times 10^5$, $\bar{M}n = 0.10 \times 10^5$, MWD = 2.6	76
$CpZrCl_3$	60	$[Zr] = 4.8 \times 10^{-5}$ M, Al/Zr = 1070, 70°C, 1.4 atm	$\bar{M}w = 0.3 \times 10^5$, $\bar{M}n = 0.11 \times 10^5$, MWD = 2.7	76
$CpZrCl_3$	5	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}w = 1.1 \times 10^5$, $\bar{M}n = 0.46 \times 10^5$, MWD = 2.4	76
$CpZrCl_3$	10	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}w = 0.7 \times 10^5$, $\bar{M}n = 0.78 \times 10^5$, MWD = 2.5	76
$CpZrCl_3$	50	$[Zr] = 3.8 \times 10^{-6}$ M, Al/Zr = 10790, 70°C, 1.4 atm	$\bar{M}w = 1.01 \times 10^5$, $\bar{M}n = 0.46 \times 10^5$, MWD = 2.2	76

for Cp_2ZrCl_2 at [Zr] 4.8 x 10^{-5} mol/L. The molecular weight distribution is about 3 for all the polymers. The poly(ethylene) obtained at the lower [Zr] is reported to have higher $\bar{M}n$ of 21000 and narrower molecular weight distribution of 2.2. For $CpZrCl_3$ initiated polymerizations it was observed that there was a slight dip of $\bar{M}n$ during the first 10 min, after which $\bar{M}n$ increases with time. This decrease of molecular weight with time during the early stages of polymerization was related to the slow activation of $CpZrCl_3$ system as compared to the Cp_2ZrCl_2 system.

1.4.6 Effect of hydrogen

Hydrogen is a well known chain transfer agent to control the molecular weights of poly(ethylene)s. The effect of hydrogen on molecular weight and catalyst activity reported by various workers is summarized in Table 1.12.

Vandenberg[77] and Natta[78] were the first to study the effect of hydrogen on ethylene polymerization on heterogeneous catalyst systems $TiCl_3/AlEt_3$, $Mg(OEt)_5$-$TiCl_4/AlEt_3$. Kaminsky and Luker[79a,79b] and Chien and Wang[76] studied the effect of hydrogen on molecular weight and catalyst activity on ethylene polymerization using Cp_2ZrCl_2/MAO catalyst system.

The catalyst activity and polymer molecular weight have been shown to decrease upon addition of hydrogen. The value of $\bar{M}n$ was reduced from 9000 (without hydrogen) to 570 (with pH_2 288 torr) whereas polydispersity increased from 3.3 to 7.9. Chain terminating effect of H_2 and formation of more active centers will give a polymer with low molecular weight and high molecular weight distribution. A linear relationship was reported between $\bar{M}v$ and the ratio of concentrations of hydrogen and ethylene.

In contrast to most heterogeneous catalysts, only traces of hydrogen are necessary to lower the molecular weight in a wide range. Kaminsky showed that $\bar{M}v$ decreases from 120000 in the absence to nearly 10000 in the presence of H_2. To reduce the

Table 1.12 Effect of Hydrogen on Ethylene Polymerization using Cp_2ZrCl_2/MAO Catalyst System

Ethylene pressure (atm)	Hydrogen (atm)	$[pH_2/pH_2+pC_2H_4]$ x 100	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Features	Reference
1.4	-	-	[Zr] = 4.8 x 10^{-5} M, Al/Zr = 1070, Temperature = 70°C	17.6	$\bar{M}n$ = 9 x 10^4, MWD = 3.3	76
1.4	0.063	4.306	[Zr] = 4.8 x 10^{-5} M, Al/Zr = 1070, Temperature = 70°C	13.2	$\bar{M}n$ = 5.1 x 10^4, MWD = 4.1	76
1.4	0.095	6.355	[Zr] = 4.8 x 10^{-5} M, Al/Zr = 1070, Temperature = 70°C	14.4	$\bar{M}n$ = 2.6 x 10^4, MWD = 5.0	76
1.4	0.38	21.304	[Zr] = 4.8 x 10^{-5} M, Al/Zr = 1070, Temperature = 70°C	13.8	$\bar{M}n$ = 0.6 x 10^4, MWD = 9.3	76
8	-	-	[Zr] = 1.5 x 10^{-6} M, Al/Zr = 11500, Temperature = 60°C	26	$\bar{M}v$ = 12.0 x 10^4	79a,b
4	0.3	6.98	[Zr] = 1.5 x 10^{-6} M, Al/Zr = 11500, Temperature = 60°C	17	$\bar{M}v$ = 1.1 x 10^4	79a,b
4	0.40	9.1	[Zr] = 1.5 x 10^{-6} M, Al/Zr = 11500, Temperature = 60°C	5	$\bar{M}v$ = 0.9 x 10^4	79a,b
8	-	-	[Zr] = 1 x 10^{-7} M, Al/Zr = 500000, Temperature = 60°C	4200	-	79a,b
8	0.096	1.2	[Zr] = 1 x 10^{-7} M, Al/Zr = 500000, Temperature = 60°C	2600	-	79a,b

molecular weight to about one half of the value obtained without hydrogen it is only necessary to feed the reactor with 7.5 vol% of H_2. Kaminsky has observed lowering of activity by the addition of hydrogen.

Based on the study of chain-transfer kinetics of ethylene polymerization with α-$TiCl_3$ and Et_3Al, Natta[78] established the relationship (Equation 1.5)

$$\frac{\bar{M}n^{\circ}}{\bar{M}n^{H}} = 1 + K\,(PH_2)^{n} \qquad (1.5)$$

where $\bar{M}n^{\circ}$ is the molecular weight of the polymer in the absence of hydrogen, $\bar{M}n^{H}$ is the molecular weight of the polymer in the presence of hydrogen, pH_2 is the partial pressure of H_2 and "k" and "n" are constants. The value of n in the exponent of equation 1.5 was reported to be 1.0 for a homogeneous catalyst system[79c,79d]. Kaminsky and coworkers[79a,79b] also reported the value of exponent of n in equation 1.5 as 1.0, for the Cp_2ZrCl_2/aluminoxane catalyst, in agreement with earlier studies[79c,79d].

1.4.7 Effect of nature of alkyl group in aluminoxane

The general formula of aluminoxane is $-[AlR-O-]_n-$ wherein

If R = methyl, the aluminoxane is MAO
If R = ethyl, the aluminoxane is ethylaluminoxane
If R = isobutyl, the aluminoxane is isobutylaluminoxane
and so on

The alkylaluminums on partial hydrolysis give corresponding aluminoxanes. It is reported that of the various aluminoxanes, MAO is more effective than ethylaluminoxane or isobutylaluminoxane. Mixed aluminoxanes are also found to be more effective as cocatalysts for the polymerization of olefins. There are very few reports in literature for comparison of the role of different aluminoxanes as cocatalysts for the polymerization of ethylene. Literature data are summarized in Table 1.13.

1.4.8 Effect of molecular weight of MAO

Trimethyl aluminum on controlled partial hydrolysis gives oligomeric aluminoxane bearing a general formula $[-AlMe-O-]_n$- Depending on the method of synthesis different researchers have reported different "n" values, ranging from 2-30. There are no reliable data in literature which reports the effect of degree of oligomerization of MAO on ethylene polymerization. The available literature data are summarized in Table 1.14. The degree of polymerization of MAO is determined cryoscopically using benzene as solvent. It is reported that the catalyst activity of bis(cyclopentadienyl)dimethyl titanium(IV) increases with the increase of degree of oligomerization of MAO for ethylene polymerization[80,81]. It has been reported that to obtain a fairly high catalyst activity the cocatalyst MAO must have a critical degree of polymerization[59]. It is observed that higher the degree of oligomerization higher the catalyst activity. The degree of polymerization of aluminoxane also has some effect on molecular weight of poly(ethylene). However, this has not been studied systematically in the literature.

1.4.9 Effect of TMA in MAO on the polymerization of ethylene

As discussed earlier, controlled and partial hydrolysis of TMA gives MAO. The unreacted TMA cannot be removed completely and there is always a small but definite amount of TMA present along with MAO. There have been only a few reports in literature which examine the role of associated TMA on the nature of catalysis. The literature data showing the effect of added TMA to MAO on the polymerization of ethylene is summarized in Table 1.15.

Very low activities have been reported in literature when TMA alone is used as cocatalyst for ethylene polymerization[61a]. The effect of free TMA on catalyst activity and molecular weight of ethylene has been studied using $(Ind)_2Zr(CH_3)_2$ and

Table 1.13 Effect of Nature of Alkyl Group in Aluminoxane for Ethylene Polymerization

Catalyst system	cocatalyst	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Features	Reference
$Cp_2Zr(CH_3)_2$	MAO	[Zr] = 1 x 10^{-7} M, Al/Zr = 50000, 70°C, 8 atm	325	-	86
Cp_2ZrCl_2	EAO	[Zr] = 1.5 x 10^{-6} M, Al/Zr = 3300, 70°C, 8 atm	50	-	86
$Cp_2Zr(CH_3)_2$	TIBDAO	[Zr] = 3 x 10^{-6} M, Al/Zr = 1700, 70°C, 8 atm	175	-	86
$Cp_2Zr(CH_3)_2$	MAO	[Zr] = 3 x 10^{-7} M, Al/Zr = 49500, 70°C, 8 atm	-	$\bar{M}n = 1.9 \times 10^5$	91
$Cp_2Zr(CH_3)_2$	PAO	[Zr] = 9.1 x 10^{-6} M, Al/Zr = 1650, 70°C, 8 atm	-	$\bar{M}n = 5.0 \times 10^5$	91
Cp_2ZrCl_2	EAO	[Zr] = 4.6 x 10^{-6} M, Al/Zr = 3300, 60°C, 8 atm	-	$\bar{M}n = 5.0 \times 10^5$	91
Cp_2ZrCl_2	MAO	[Zr] = 1.1 x 10^{-6} M, Al/Zr = 15450, 70°C, 1.4 atm	345	-	76

MAO = methylaluminoxane, EAO = ethylaluminoxane, TIBDAO = tetraisobutyl dialuminoxane, PAO = isopropyl aluminoxane

Table 1.14 Effect of MAO Degree of Polymerization (D.P) on Ethylene Polymerization

Catalyst system	D.P.	Polymerization conditions	Activity (Kg-PE/g-met.h.atm)	Features	Reference
$Cp_2Ti(CH_3)_2$	2	[Zr] = 13.4 x 10^{-5} M, 20°C, 120 min	0.0082	-	80
$Cp_2Ti(CH_3)_2$	5	[Zr] = 13.4 x 10^{-5} M, 20°C, 120 min	2.09	$\bar{M}v$ = 3.6 x 10^5	80
$Cp_2Ti(CH_3)_2$	10	[Zr] = 13.4 x 10^{-5} M, 20°C, 120 min	2.54	$\bar{M}v$ = 1.2 x 10^5	80
$Cp_2Zr(CH_3)_2$	10-12	[Zr] = 1 x 10^{-8} M, Al/Zr = 1600000, 70°C	4450	$\bar{M}v$ = 1.78x 10^5	80
$Cp_2Zr(CH_3)_2$	12	[Zr] = 1 x 10^{-7} M, Al/Zr = 148000, 70°C	5800	$\bar{M}v$ = 1.43 x 10^5	80
$Cp_2Zr(CH_3)_2$	14	[Zr] = 1 x 10^{-7} M, Al/Zr = 153000, 70°C	6250	$\bar{M}v$ = 1.66 x 10^5	80
$Cp_2Zr(CH_3)_2$	14	[Zr] = 1 x 10^{-7} M, Al/Zr = 150000, 70°C	7450	$\bar{M}v$ = 1.5 x 10^5	81
$Cp_2Zr(CH_3)_2$	25-28	[Zr] = 3 x 10^{-7} M, Al/Zr = 14140, 50°C	108	$\bar{M}v$ = 3.3 x 10^5	59

Table 1.15 Effect of TMA in MAO for the Polymerization of Ethylene using Metallocene/MAO Catalyst System

Catalyst	[TMA].10^2 M (Al)	[MAO].10^2 M (Al)	TMA/ MAO	Polymerization conditions	Activity (Kg-PE/g-Zr.h.atm)	Features	Reference
Cp_2ZrCl_2	0	5.14	-	Al/Zr = 1070, 70°C, 1 atm	25	[η] = 0.47 dL/g, $\overline{M}v$ = 1.1 x 10^4	82
Cp_2ZrCl_2	2.57	2.57	1	Al/Zr = 1070, 70°C, 1 atm	18	[η] = 0.44 dL/g, $\overline{M}v$ = 1.0 x 10^4	82
Cp_2ZrCl_2	3.43	1.71	2	Al/Zr = 1070, 70°C, 1 atm	15	[η] = 0.43 dL/g, $\overline{M}v$ = 0.98 x 10^4	82
Cp_2ZrCl_2	4.67	0.47	10	Al/Zr = 1070, 70°C, 1 atm	15	[η] = 0.31 dL/g, $\overline{M}v$ = 0.66 x 10^4	82
Cp_2ZrCl_2	5.04	0.1	50	Al/Zr = 1070, 70°C, 1 atm	8.1	[η] = 0.18 dL/g, $\overline{M}v$ = 0.33 x 10^4	82
Cp_2ZrCl_2	5.09	0.05	100	Al/Zr = 1070, 70°C, 1 atm	8.3	[η] = 0.36 dL/g, $\overline{M}v$ = 0.79 x 10^4	82
Cp_2ZrCl_2	5.12	0.017	300	Al/Zr = 1070, 70°C, 1 atm	1.2	[η] = 0.25 dL/g, $\overline{M}v$ = 0.5 x 10^4	82
Cp_2ZrCl_2	5.14	0.005	1000	Al/Zr = 1070, 70°C, 1 atm	0.2	[η] = 0.26 dL/g, $\overline{M}v$ = 0.52 x 10^4	82
Cp_2ZrMe_2	0.5	0	-	Al/Zr = 500, 570°C, 4 atm	0.0042	[η] = 2.6 dL/g	61a
Cp_2ZrPh_2	0.5	0	-	Al/Zr = 500, 50°C, 4 atm	0.0054	[η] = 3.3 dL/g	61a
$Cp_2Zr(CH_2Ph)_2$	0.5	0	-	Al/Zr = 500, 50°C, 4 atm	0.0084	[η] = 2.7 dL/g	61a
$Cp_2Zr(CH_2SiMe_3)_2$	0.5	0	-	Al/Zr = 500, 50°C, 4 atm	0.0024	[η] = 3.6 dL/g	61a

$Cp_2Zr(CH_2C_6H_5)_2$ along with MAO[69]. Catalyst activity have been found to decrease with increasing [TMA]/[MAO] ratios. Molecular weights of the poly(ethylene) obtained with $Cp_2Zr(CH_2C_6H_5)_2$ strongly decrease with increasing TMA, whereas it has been reported to be invariant when $(Ind)_2Zr(CH_3)_2$ is used. Ethylene polymerization with Cp_2ZrCl_2/MAO has been investigated by progressively replacing MAO with TMA. The polymerization rate and polymer yield were reduced only by a third to a fourth when 99% of MAO was replaced with TMA and the polymer molecular weights are unaffected for $[TMA]/[MAO] \leq 2$ and is lowered by 40% ($\bar{M}v$ = 11000 to 6600) at a [TMA]/[MAO] ratio of 10. The kinetic profile of Cp_2ZrCl_2/MAO and Cp_2ZrCl_2/MAO+TMA are very similar for $[TMA]/[MAO] \leq 10$. The initial rate of polymerization is large followed by decay to about half the rate. When [TMA]/[MAO] = 100, there is a period of Rp build up reaching a constant value which is about 60% of the asymptotic value of Rp for MAO alone as the cocatalyst. With increasing addition of free TMA to MAO, both catalyst activity and molecular weight decrease[82]. Unfortunately, the literature in this area is rather difficult to interpret as various researchers use MAOs prepared by different methods, which are not completely characterized. The free TMA content in MAO is hardly reported in published literature.

1.4.10 Kinetics and mechanism of polymerization

1.4.10.1 Kinetics of polymerization

Even after 40 years of its discovery the Ziegler-Natta catalysts have not lost their fascination till today and although widely applied, reaction mechanisms are not yet completely understood.

Polymerization of ethylene catalyzed by homogeneous and highly alkylated Ziegler-Natta catalysts, based on bis(cyclopentadienyl)titanium-IV or zirconium-IV compounds and trialkylaluminums, consists of a series of reactions which involve the formation of inactive catalysts and which greatly complicate the kinetic interpretation of the polymerization. A scheme showing these side reactions is given in Figures 1.1, 1.2 and 1.3.

Concomitant with continued olefin insertion into the metal-carbon bond of the titanium or zirconium-aluminoxane complex, alkyl exchange and hydrogen transfer reactions are observed[84,86]. Usually the normal reduction mechanism for the formation of metal hydride is followed by a hydride-transfer to an alkyl group. In case of some titanium and zirconium compounds a reverse reaction takes place. The central atom in the metal-CH_2-CH_2-metal structure is reduced by separation of ethylene. It has been reported that in the case of zirconium system the above discussed side reaction is very slow because of the much greater resistance of the zirconium to reduction[79a,79b,86].

The increase of polymerization activity by addition of water to the homogeneous catalysts[24,25] can be explained either by the presence of a higher percentage of active centers (based on the amount of transition metal) or by a higher insertion velocity (velocity constant). The reported kinetic data for some Ziegler-Natta catalysts are shown in Table 1.16[85].

For soluble systems comprising of Cp_2ZrCl_2/MAO or Cp_2ZrMe_2/MAO the value of C^* is 1 which indicates that practically every transition-metal atom is active. The above mentioned side reactions are reported to be low in the case of aluminoxane cocatalyzed polymerizations[9]. Typical ethylene polymerization kinetic profiles for the zirconocene/MAO and titanocene/AlR_3 catalysts systems are shown in Figure 1.12.

For the Cp_2ZrCl_2/MAO the maximum rate of polymerization, Rp is reached within a minute after introduction of the catalyst followed by a modest decay of Rp to about half of the rate. Rp is reported to be high at lower [Cp_2ZrCl_2] or higher [Al]/[Zr] ratio[76].

Table 1.16 Comparison of the Effective Polymerization Rates ($k_p .C^*$) of Different Ziegler-Natta Catalysts for the Polymerization of Ethylene

Catalyst system	$k_p .C^*$ (Lit/mol.sec)	C^* (mol/mol)	E_A (KJ/mol)	Temp. (°C)
$TiCl_3/AlEt_2Cl$	2.7	0.005	71	50
$TiCl_4/AliBu_3$	0.5	0.03	42	30
$TiCl_4/MgBuBr/AlEt_3$	350	0.6	75	50
$TiCl_4/Mg(OEt)_2/AlEt_3$	70	0.7	-	70
$TiCl_4/RMgCl_3/AlEt_3$	6000	0.4	-	70
Cp_2ZrCl_2/MAO	10000	1	-	60
$Cp_2Zr(CH_3)_2/MAO$	100000	1	75	90

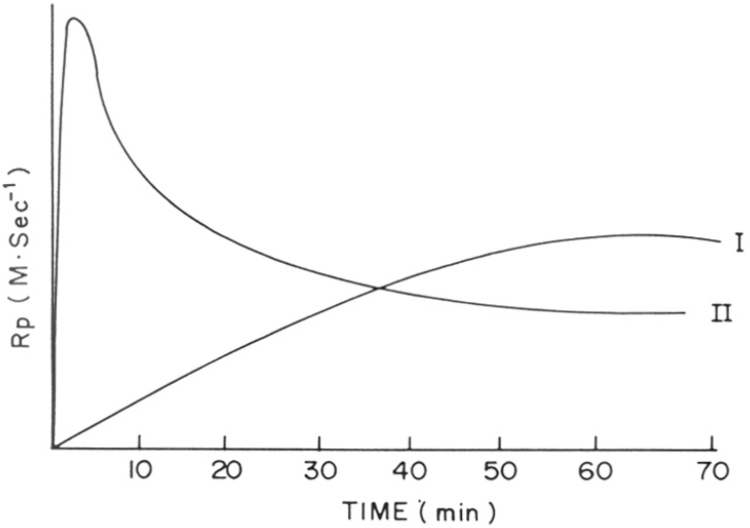


Fig. 1.12 Typical rate curves for Cp_2TiCl_2-AlR_3 (I) and Cp_2ZrCl_2-MAO (II) catalyzed ethylene polymerization

It has been reported that the number of active sites $[C^\bullet]$, lie between 75 and 100% of the Zr compounds. Therefore activity should be independent of [Zr][76]. But in reality activity is found to increase with the decrease of catalyst concentration. This is due to the increase of $\mathbf{k}_p$ (rate constant of propagation). The activity has been found to be proportional to the $[Cp_2ZrCl_2]^{-0.77}$ when log-log of activity versus $[Cp_2ZrCl_2]$ is plotted. This indicates faster propagation at low $[Cp_2ZrCl_2]$.

Kaminsky et al[73]., as well as Chien and Wang[76] have reported that zirconocene/MAO catalysts must exist in at least two active forms. These active species will differ by the number of MAO molecules complexed to them[76]. Depending upon the number of MAO molecules complexed to active species $\mathbf{k}_p$, rate constant for propagation will vary. Chien and Wang have experimentally shown that high activity for low [Zr] and large [MAO] indicate higher $\mathbf{k}_p$ for species having larger content of complexed MAO i.e., larger Al/Zr ratios. The plot of Rp versus time for different Al/Zr ratios is shown in Figure 1.11.

The activity of the Cp_2ZrCl_2/MAO catalyst as a function of temperature for ethylene polymerization has been reported by various authors[59,76]. Activity has a broad maximum between 30 and 80°C; it decreases at both higher and lower temperatures. This may be attributed to increase of both propagation and deactivation with increasing temperature. The deactivation is reported to follow first order kinetics[76]. The slow dissociation of complexed MAO is one way of deactivation. (Equation 1.6)

$C_i^\bullet\text{-P} \dashrightarrow C_{i-n}^\bullet\text{-P} + n\ \text{MAO}$ (1.6)

Where, $C_i^\bullet$ = Active center complexed with "i" number of MAO

The $C_i^\bullet - 1$ is less protected by MAO than $C_i^\bullet$ and in fact if i-n = 0, rapid bimolecular deactivation equation follows, as

$P = [M]\Sigma\ kp\ [C^\bullet_{i},o](1-e^{-Kd,it})$ (1.7)

where P = activity

A second possible mechanism is via β-hydride elimination to give metallocene hydride which shows very low propensity for monomer insertion. Another possibility is the elimination of a poly(ethylene) molecule having three carbon atoms less than the propagating Zr-P and the latter fragment remains as a $\eta\underline{3}$:allyl group complexed to Zr rendering the Zr inactive for ethylene polymerization. It is reported that MAO has the dual functions of enhancing the polymerization activity as also to inhibit the reduction of transition metal.

Kinetic studies were reported by Tsutsui and Kashiwa for ethylene polymerization with Cp_2ZrCl_2 in conjunction with MAO at a Al/Zr = 500 (5×10^{-6} mol/L) using toluene and n-decane at 30°C for a short time[83]. The concentration of active centers $[C^*]$ and the polymerization rate constant kp were greatly dependent on the solvent, that is 1 mol/mol Zr and 1700 Lit/mol. s in toluene and 0.6 mol/mol Zr and 300 Lit/mol. s in n-decane. The polymerization rate was observed to be constant within 6 min from the beginning of polymerization, and then rate decay starts.

Apart from these parameters, the rate of polymerization is also dependent on the manner of addition of the catalyst and the cocatalyst, monomer concentration, ageing time and pressure.

1.4.10.2 Nature of active center and mechanism

Electrodialysis, Chemical trapping, XPS, surface chemical, NMR spectroscopic and theoretical studies argue indirectly that the role of the Lewis acid (AlR_3 or aluminoxane) is to promote (e.g., by alkide abstraction) formation of unsaturated "cation-like" active centers (e.g., Cp_2MR^+). Primary reaction step for the formation of active center is methylation of the transition metal compound by MAO. The active sites and mechanism proposed by different researchers for ethylene polymerization are best discussed under the following subheadings.

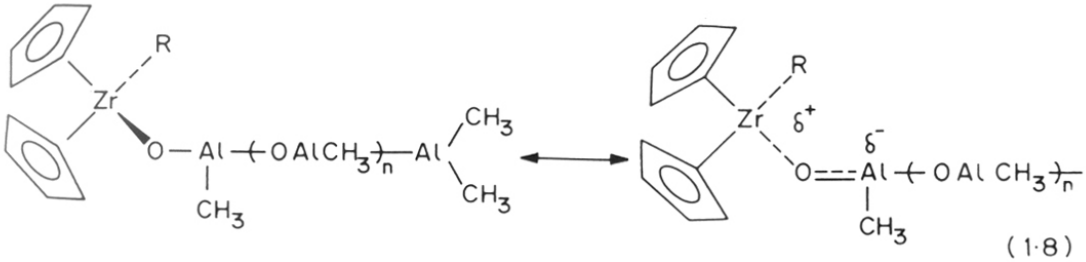
- i) Kaminsky's model
- ii) Giannetti's model
- iii) Chien's model
- iv) Giannini's model

i) Kaminsky's model

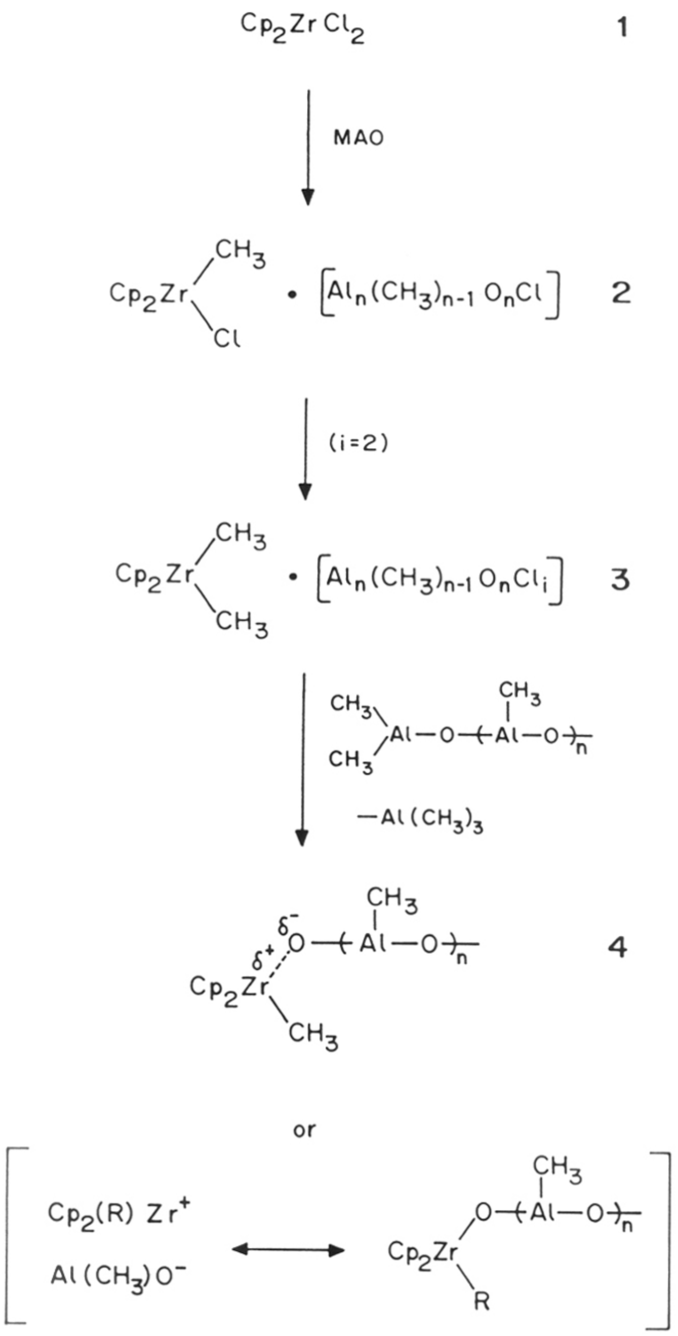
The formation of an UV active complex has been reported by Kaminsky *et al.* between Cp_2ZrCl_2 and MAO. With the help of ^{1}H-NMR studies they have reported that after methylation of zirconium compound MAO further reacts with $Cp_2ZrMeCl$ to form further complexes by loss of methane[86,89,90]. This aspect is further discussed in nature of deactivation section 1.4.10.3. Zr-O-Al structure was evidenced by EXAFS studies. Based on the ^{1}H-NMR studies and EXAFS measurements Kaminsky et al[90]., proposed a Scheme (Scheme 1.1) for the formation of active center.

ii) Gianetti's model

Based on UV experiments and molecular orbital theory Giannetti has proposed an active center containing Zr-O-Al linkage. The active species proposed by Giannetti is a highly polar structure[59]. (Equation 1.8)



(1·8)

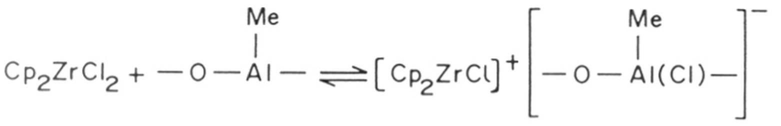


Scheme 1.1 Mechanism showing the formation of active center for the Cp_2ZrCl_2-MAO catalyst system

iii) Chien's model

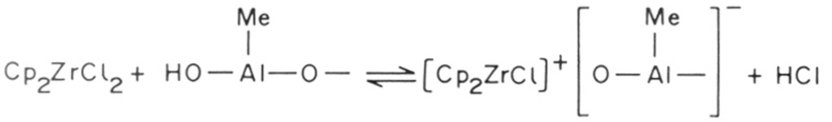
Chien has proposed two kinds of active species $C_i^{\bullet}$ and $C_i^{\bullet +}$ for the Cp_2ZrCl_2/MAO system[76], depending on "i" number of MAO molecules complexed to $C^{\bullet}$. It is difficult to determine the structures of these species because both the molecular weight and molecular weight distribution of MAO are unknown and can differ with the method of synthesis. Also, it will depend on whether MAO is an uni-, bi-, or multi-dentate ligand. Therefore, "i" really corresponds to the number of coordination positions of the transition metal occupied by MAO. Under conditions which show significantly less than quantitative amount of active species by radiolabelling experiment, say 75% of [Zr], it is possible that there is 25% of $C_i^{\bullet}$ with $i = 0$ which deactivates rapidly. Based on the increase of kp with decrease of [Zr] and increase of [Al]/[Zr], Chien has proposed that $C_2^{\bullet}$ ($i = 2$) is the most active and stable species whereas $C_1^{\bullet}$ (where $i = 1$) has an intermediate activity and stability. According to Chien MAO has the dual functions of enhancing the intrinsic polymerization activity and to inhibit the reduction of transition metal.

$C^{\bullet +}$ produced by reaction of Cp_2ZrCl_2 with MAO



$$\mathrm{Cp_2ZrCl_2} + -\mathrm{O}-\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}- \rightleftharpoons [\mathrm{Cp_2ZrCl}]^{+}\left[-\mathrm{O}-\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}(\mathrm{Cl})-\right]^{-} \qquad (1{\cdot}9)$$

Alternatively, the reaction may be between Cp_2ZrCl_2 and the hydroxy group of MAO



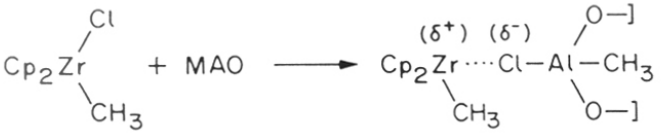
$$\mathrm{Cp_2ZrCl_2} + \mathrm{HO}-\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}-\mathrm{O}- \rightleftharpoons [\mathrm{Cp_2ZrCl}]^{+}\left[\mathrm{O}-\overset{\mathrm{Me}}{\overset{|}{\mathrm{Al}}}-\right]^{-} + \mathrm{HCl} \qquad (1{\cdot}10)$$

Alkylation of this complex by MAO yields $C^{\bullet +}$ which is complexed to MAO.

iv) Giannini's model

The interaction of Cp_2ZrCl_2 with MAO has been studied by ^1H-NMR spectroscopy. Giannini and Cam report that Cp_2ZrCl_2 is monoalkylated by TMA present in MAO[60]. The TMA contained in MAO is proposed to be the active species in the alkylation of Cp_2ZrCl_2 (Equation 1.11). The $Cp_2Zr(CH_3)Cl$ is proposed to form, with an excess of MAO, a highly polarized active species (Equation 1.12).

$$\begin{aligned} Cp_2ZrCl_2 + MAO.xAl(CH_3)_3 \text{ --> } & (1\text{-}x)Cp_2ZrCl_2 + Cp_2Zr(CH_3)Cl \\ & + MAO.xAl(CH_3)_2Cl \qquad (1.11) \end{aligned}$$



(1.12)

Based on above evidences and models the active species can be best represented as structure-4 shown in Scheme 1.1. However, this structure should be considered as an over simplified depiction of the true active center. The influence of MAO is not just limited to alkylation and coordination of the metallocene. Obviously, there is a need to seek additional explanations for explaining the unique cocatalytic activity of MAO. This aspect is more extensively discussed in Chapter IV.

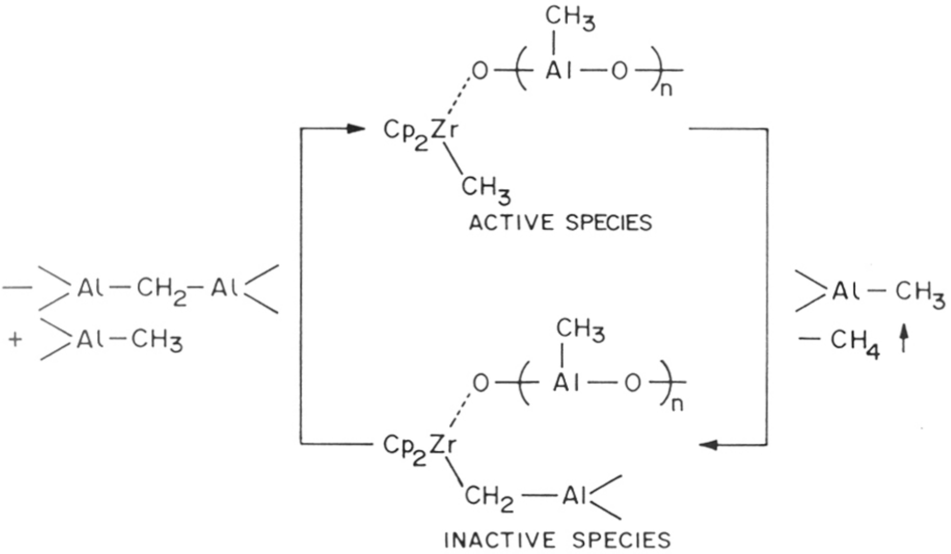
1.4.10.3 Nature of deactivation processes

Inspite of extensive published data on the MAO cocatalyzed α-olefin polymerization, the role of MAO activators and the origin of catalyst deactivation are not fully understood. A complex formation between the transition metal and cocatalyst MAO and subsequent alkylation of the transition metal is the first step for the formation of the active species.

The alkyl exchange reaction is a reversible one and besides this an irreversible dealkylation takes place which leads to the deactivation of the active species[8](eg: active titanium(IV)- species to deactive titanium(III) in the case of $Cp_2Ti(IV)$-based systems) (Figure 1.2). Most titanium(IV)- compounds tend to be reduced by alkylaluminum in a very complicated sequence of reactions, accompanied by evolution of alkane and alkene. Kaminsky and Sinn[28] have studied the reduction process most thoroughly. They have shown that the first step of reduction is transfer of a β-hydrogen atom of one alkyl group to the other with the formation of metal-CH_2-CH_2-metal structures (Figure 1.1). These dimetallo alkanes in the titanium systems are unstable and decompose by "ethylene splitting" into trivalent titanium compounds. The reduced titanium complex is no longer active for ethylene polymerization[28].

Based on ^1H-NMR studies Kaminsky et al[90]., reported a deactivation process where the formation of inactive Zr-CH_2-Al structure was shown by the evolution of methane (Scheme 1.2). In presence of excess of MAO this inactive Zr-CH_2-Al structure is converted into active Zr-CH_3 by transmetallation reaction with the loss of Al-CH_2-Al structure.

Recently, the kinetics of propylene polymerization was studied by Fisher and Mulhaupt in the presence of homogeneous Cp_2ZrCl_2/MAO catalysts in toluene at 2 bar at 0,20,40 and 60°C[92]. Activation of Cp_2ZrCl_2 complex by alkylation with MAO, involves a very fast reaction yielding the catalytically active sites. At a reaction temperature of 40°C Fisher and Mulhaupt observed rapid decay for propylene polymerization. Similar rapid decay has been observed in ethylene polymerization involving homogeneous metallocene catalysts[76]. Based on polydispersities (>2) Chien and Wang[76] proposed the presence of two different catalytically active sites which are deactivated in processes that are first order with respect to the individual catalytically active site concentrations. Based on polydispersities (<2) in low molecular weight range for propylene polymerization Fisher and Mulhaupt conclude that the active sites are uniform over the entire temperature range.



Scheme 1.2 Mechanism showing the deactivation of the active center for the Cp_2ZrCl_2-MAO catalyst system

At a given monomer concentration the actual polymerization rate Rp is proportional to the concentration of the catalytically active sites N^{*}[93] (Equation 1.13)

$$R_p \sim N^{*} \qquad (1.13)$$

In a two step deactivation process, the catalytically active complexes C^{*} are deactivated by a reversible followed by an irreversible process to form inactive species I_1 and I_2[92]. (Equation 1.14)

Only I_1 can recover and again take part in propylene polymerization.

$$2C^{*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \xrightarrow{k_2} I_2 \qquad (1.14)$$

Alkylation and dealkylation reversible reaction can be compared to the above equilibrium reaction between C^{*} and I_1 and reduction of the transition metal i.e., formation of inactive species can be compared to the formation of I_2.

In the initial phase of the polymerization reaction only active centers C^{*} are present, and these form I_1 and I_2. Below 40°C for propylene polymerization reaction the rate constant K_2 is very small. Therefore, in an approximation, Fisher and Mulhaupt[92] suggested that a simplified equilibrium shown in Equation 1.15 is responsible for the decay of the catalytically active center concentration N^{*}, which was calculated by Mauser's method[94]. (Equations 1.16 to 1.19)

$$2C^{*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \qquad (1.15)$$

$$N^{*}(t) = N^{*}_{\infty} + \frac{(N^{*}_{0} - N^{*}_{\infty})\, r \exp(-rt)}{r + 2k_{1}(N^{*}_{0} - N^{*}_{\infty})(1-\exp(-rt))} \qquad (1\cdot16)$$

$$N^{*}_{0} \equiv N^{*}_{t=0} \qquad (1\cdot17)$$

$$N^{*}_{\infty} \equiv N^{*}_{t\rightarrow\infty} = \frac{1}{2}\left[\sqrt{\left(\frac{k_{-1}}{2k}\right)^{2} + 2\frac{k_{-1}}{k_{1}}N^{*}_{0}} - \frac{1}{2}\frac{k_{-1}}{k_{1}}\right] \qquad (1\cdot18)$$

$$r \equiv \sqrt{k_{-1} + 8k_{1}k_{-1}N^{*}_{0}} \qquad (1\cdot19)$$

It was proposed that the irreversible deactivation in propylene polymerization for Cp_2ZrCl_2 system is a second order reaction with respect to the catalytically active metallocene complexes.

1.4.11 Supported metallocenes

Though homogeneous metallocene-MAO catalyst system are well known for their high activities, good copolymerization activities, narrow polydispersities, and excellent control on stereoregularity, they suffer from some drawbacks, from the point of view of practical catalysis, such as, inability to use the catalyst in gas phase or slurry processes and poor control of polymer morphology. One of the methods available in the literature to overcome these drawbacks is to support the metallocene on inorganic supports such as, silica, alumina or magnesium chloride with or without MAO. The available literature data on the supported metallocenes is summarized in Table 1.17.

Table 1.17 (a) Supported Metallocene Catalysts for Propylene Polymerization

Catalyst system	Polymerization conditions	Activity (Kg-PP/mol-Zr.h.atm)	Features	Reference
$MgCl_2/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$ - $Al(CH_3)_3$	Pressure = 1 atm Temperature = 40°C Time = 18 h	19.7	$\bar{M}n$ = 1590, MWD = 4.2	95
$Al_2O_3/Al(CH_3)_3/Et[IndH_4]_2ZrCl_2$ - $Al(CH_3)_3$	Pressure = 1 atm Temperature = 40°C Time = 18 h	14.4	$\bar{M}n$ = 1730, MWD = 2.4	95
$Al_2O_3/Al(CH_3)_3$/iPr(Flu)(Cp)$ZrCl_2$-$Al(CH_3)_3$	Pressure = 1 atm Temperature = 40°C Time = 18 h	9.2	$\bar{M}n$ = 4600, MWD = 2.0, Syndiotacticity = 86%	97
$Al(CH_3)_3$/Partially dehydroxylated alumina/Et(Ind)$_2ZrCl_2$ - MAO	Pressure = 5 atm Temperature = 300°C Time = 1.5 h	0.6	$\bar{M}n$ = 19500, MWD = 1.61, Syndiotacticity = 90%, Tm = 143°C	98
MAO/$SiO_2/Et[IndH_4]ZrCl_2$ - $Al(C_2H_5)_3$	Pressure = 1 atm Temperature = 40°C Time = 1 h	43.3	$\bar{M}n$ = 5300, MWD = 2.5, Isotacticity = 90%, Tm = 127°C	95

Table 1.17 (b) Supported Metallocene Catalysts for Ethylene Polymerization

Catalyst system	Polymerization conditions	Activity (Kg-PE/mol-Ti.h.atm)	Features	Reference
$(C_2H_5)_nAlCl_{3-n}/SiO_2/Cp_2TiCl_2$-$(C_2H_5)_nAlCl_{3-n}$	Pressure = 1 atm Temperature = 20°C Time = 0.5 h	Activity value is not reported	Broadening of MWD by GPC observed	112
$MgCl_2/Cp_2TiCl_2$ - $Al(iBu)_3$	Pressure = 1 atm Al/Ti = 50 Temperature = 40°C Time = 1 h	2.5	Rp = 0.39 M/Sec [η] = 2.6 dL/g (in ODCB at 135°C)	104
$MgCl_2/Cp_2TiCl_2$ - $Al(iBu)_3$	Pressure = 1 atm Al/Ti = 100 Temperature = 60°C	2.0	Rp = 0.76 M/Sec [η] = 1.37 dL/g (in ODCB at 135°C)	104
$MgCl_2/Cp_2TiCl_2$ - MAO	Pressure = 1 atm Al/Ti = 1000 Temperature = 40°C Time = 1 h	156	Rp = 72 M/Sec [η] = 1.81 dL/g (in decalin at 135°C)	105
$MgCl_2/Cp_2TiCl_2$ - MAO	Pressure = 1 atm Al/Ti = 500 Temperature = 60°C Time = 0.5 h	219	Rp = 74 M/Sec [η] = 1.91 dL/g (in decalin at 135°C)	105

Physical mixing of support and metallocene is one of the preparative route employed to synthesize these catalysts. Kaminaka and Soga were the first to screen systematically the efficiency of different supports by preparing supported ethylenebis(tetrahydroindenyl) zirconium(IV)dichloride catalyst for the isospecific polymerization of propylene[95-97]. Alumina, silica and $MgCl_2$ pretreated with MAO were used as supports and trialkylaluminum as cocatalyst. Al_2O_3 and $MgCl_2$ gave low molecular weight polymers with broad polydispersity. On the contrary, SiO_2 pretreated with MAO gave narrow polydispersities and low catalyst activity. Recently, Chien and He[98] and Collins[99] *et al.* have shown that isospecific polymerization of propylene can be performed with supported chiral ansa-metallocenes in conjunction with MAO. More recently, Kaminsky and Remner have shown a refined route for preparation of silica supported ansa-metallocene catalyst which yields high molecular weight, high melting poly(propylene) with a performance similar to heterogeneous catalysts[100]. All these catalysts were prepared by physical mixing of support with zirconium compounds in a diluent such as toluene. A $MgCl_2$ supported Cp_2ZrCl_2 catalyst has also been reported for the polymerization of ethylene[101-103]. Satyanarayana and Sivaram have reported recently a new preparative route to $MgCl_2$ supported Cp_2TiCl_2 catalyst by exploiting the solubility of $MgCl_2.2THF$ complex and Cp_2TiCl_2 in THF[104]. This catalyst showed significant activity for ethylene polymerization in presence of trialkylaluminum and was capable of yielding polymers with high molecular weights. In presence of MAO the same catalyst system was reported by Sarma *et al.* to yield high catalytic activities for the polymerization of ethylene at low Al/Ti ratios[105].

1.5 Metallocene catalysts for olefin polymerization: Industrial Processes

Metallocene catalysts for polyolefins have been under development for ten years and are now in the early stages of commercialization. Todate the leading ten or so companies in the field have been awarded around 200 patents (Table 1.18 gives

Table 1.18 Representative Patent Literature of Homopolymerization of Ethylene using Homogeneous Ziegler-Natta Catalysts

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
JP 01,259,004	112:159190q	Mitsui Toatsu Chemicals, Inc.	bis[(3-trimethoxy silyl propyl)indenyl] zirconium dichloride, silica, methylaluminoxane	catalyst efficiency: 4.4x10^6 g/mol. Zr. h
EP 348,126	112:199342x	Exxon Chemical Patents, Inc.	bis(butyl cyclopentadienyl) zirconium dichloride, methylaluminoxane	catalyst activity: 885 kg/ g-Zr-h-bar
EP 383,255	114: 24783f	Idemitsu Kosan Co., Ltd.	bis(cyclo pentadienyl) zirconium dichloride, methylaluminoxane	Activity = 265 g/g-Zr.
Int. Appl. WO 9102012	114:247980u	Exxon Chemical Patents, Inc.	bis(cyclopentadienyl) hafnium di-Me tributyl ammonium tetrabis(penta fluoro phenyl)boron	molecular weight 1,123,000 M.W.D. = 1.78

Contd....

Table 1.18 Contd....

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
Ger (East) DD 282013	114: 229625c	VEB Chemische Werke Buna	4-(chloromethyl)styrene divinylbenzene copolymer titanocene dichloride homogenate, triisobutylaluminum, titaniumtetrachloride	ultra high molecular weight polyethylene obtained
EP 399348	115:30104x	Hoechst, A.-G.	[(dimethyl silylene)bis (1-inden-1-yl)] zirconium dichloride, methylaluminoxane	viscosity =0.323 ml/g bulk d. = 0.210 av. particle size 50 µm.
CCA 2022566	115:115262x	Enichem Anic S.P.A.	bis(cyclopentadienyl) Zirconium dichloride, trimethylaluminum, $Me_3SnOSnMe_3$	Activity = 220 kg/mol-Zr-h mol. wt. 36,000
EP 413,326	115:136979b	Hoechst, A.-G.	methylethylene-bis- (1-indenyl) Zirconium dichloride, methylaluminoxane	viscosity 390 cm^3/g

Contd....

Table 1.18 Contd....

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
EP 435,514	115:160013c	BP Chemical Ltd.	$MgCl_2$, diisoamylether, butanol, zirconocene, aluminoxane	M.W.D.. = 2.3 melt index = 3.9 g/10 min (2.16 kg/190^{0}C)
JP 03,103,407	115: 160019j	Idemitsu Kosan Co., Ltd.	$(Al(CH_3)_3$, iso-Bu_3Al treated with $CuSO_4.5H_2O)$ product aluminoxane, zirconocene	Activity = 34 kg/mmol. Zr/h melt index 0.5
Int. Appl. WO 9109882	115: 256897V	Exxon Chemical Patents, Inc.	bis(cyclopentadienyl) dimethyl hafnium, $PhNMe_2HB(C_6H_5)_4$, Al_2O_3	$\bar{M}w$ = 594,000 M.W.D = 2.15
PCT Int. Appl. WO 9114713	116: 42216u	Exxon Chemical Patents, Inc.	bic(cyclopentadienyl) zirconium tetrakis(pentafluoro phenyl)boron, triethylboron	M.W.D. = 1.98 $\bar{M}w$ = 449,000

Contd....

Table 1.18 Contd....

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
JP 03,234,709	116: 60207w	Mitsui Petrochemical Ind., Ltd.	bis(cyclopentadienyl) dimethyl zirconium, silica, tributylammonium tetra(p-tolyl)borate	bulk d. 0.39 melt flow rate = 0.55 g/10min M.W.D. = 2.7
EP 459320	116: 84396h	Hoechst, A.-G.	dichloro dicyclopentadienyl zirconium, dichloromethane, methylaluminoxane	M.W.D. = 2.9 $\bar{M}w$ = 670,000
JP 04,11,604	116: 174977c	Mitsui Petrochemical Ind., Ltd.	bis(butyl cyclopentadienyl) zirconiumdichloride, methylaluminoxane, silica, triisobutylaluminum	melt flow rate = 0.42 g/10min (2.16 kg/190^{0}C)
JP 0408704	116: 195079b	Mitsui Petrochemical Ind., Ltd.	bis(n-butylcyclopentadienyl) zirconiumdichloride, methylaluminoxane, triisobutylaluminum, SiO_2	bulk d. 0.40 g/mL melt flow rate 0.53 g/10 min

Contd....

Table 1.18 Contd....

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
JP 0446906	117: 8697n	Tosoh Akzo K.K.	tetraisobutylaluminoxane, trimethylaluminum, water, bis(cyclopentadienyl) zirconiumdichloride	yield = 40.11 kg/mol.Zr.h
JP 0449293	117: 8699q	Idemitsu Kosan K.K.	bis(cyclopentadienyl) zirconiumdichloride, methylaluminoxane	yield = 278 kg/g.Zr
JP 0496908	117: 91014f	Mitsui Sekiyu Kagaku Kogyo K.K.	bis(methylcyclopentadienyl) zirconiumdichloride, trimethylaluminum, silica, aqueous $MgCl_2$	narrow M.W.D. bulk d. 0.49 melt index = 0.07 g/10 min (190^0C.2.16 kg)
WO 9209640	117: 251983b	Idemitsu Kosan Co., Ltd.	ferrocenium tetrakis(penta fluoro phenyl)borate, triisobutylaluminum	M.W.D. = 3.99 $\bar{M}w$ = 1,93,000

Contd....

Table 1.18 Contd....

Patent No.	C.A. No.	Name of Company	Catalyst Composition	Features
EP 496193	118: 81632n	Hoechst, A.-G.	(vinyl cyclopentadienyl) lithium, trichloropentadienyl zirconium, AIBN, methylaluminoxane	yield = 41.4 kg/mmol.Zr.h
JP 04,275,311	118: 102938n	Idemitsu Petro Chemical Co., Ltd.	$Mg(OR)_2$, Zirconocene, Methylaluminoxane	activity 2 kg polymer/ mmol.Zr.h
PCT Int. Appl. WO 9214766	118: 125257a	Exxon Chemical Patents, Inc.	dimethylsilylbis(tetra hydroindenyl) zirconiumdichloride, methylaluminoxane, glycerol monooleate	color less dry polymer activity = 3600 kg/g.cat

representative patent literature data) on metallocene use in polyolefins with Mitsui and Exxon holding some 50 patents each[106]. The first commercial use of metallocene catalyst was announced by Exxon in their "Exxpol" solution process for the manufacture of poly(ethylene)s. Table 1.19 lists some of the major commitments for polyolefins production using metallocene catalysts[106].

The polyolefins produced by metallocenes significantly differ from the polymers produced by conventional Ziegler-Natta catalysts. Some typical properties of Exxon's Exxpol Exact poly(ethylene) resins manufactured using metallocene catalysts and their comparison with conventional resins are shown in Table 1.20[107]. Very high activity in combination with no or only a small chlorine content of metallocene catalyst systems is quite favorable from a technical point of view because no additive is necessary to prevent corrosion of the machinery during pelletizing and processing. New types of olefin homopolymers and copolymers so far not accessible can be synthesized e.g., those of ethylene with cyclic olefins. The copolymers based on ethylene and norbornene are now being test marketed by Mitsui Petrochemicals, Nipon Zeon and JSR[108]. These copolymers can effectively compete with ABS, polycarbonates, acrylic and thus push polyolefins into areas of speciality applications. These new ethylene copolymers have better UV resistance, are optically clear and have superior water absorption properties[108].

Properties of poly(ethylene) produced by metallocenes using different processes are compared in table 1.21. A comparison of the properties of gas phase LLDPE (containing hexene-1 comonomer) produced by using supported metallocenes is made with that of LLDPE obtained by conventional Ziegler-Natta catalyst in Table 1.22.

Depending on the nature of the ligands around the metal, metallocenes can provide access to poly(propylene)s with different stereospecificities, namely, isotactic poly(propylene), syndiotactic poly(propylene) or modified isotactic poly(propylene) with properties different from those produced by conventional Ti-Al catalysts[109].

Table 1.19 Worldwide Metallocene Polyolefins Capacity Commitments

Company	Region	Year of commercialization	Capacity (tonne/year)
Polyethylene			
Dow	US	1993	50000
Exxon	US	1995	100000
Mitsui	Japan	1995	100000
Mitsubishi	Japan	1994	100000
Union Carbide	US	1995	300000
Polypropylene			
Chisso	Japan		20000
Exxon	US	1996	100000
Hoechst	Europe	1995	100000
Mitsui Toatsu	Japan	1994-95	75-100000

Table 1.20 Comparison of Properties of LLDPE's Produced by Metallocene Catalysts and Conventional Ziegler-Natta Catalysts

Property	Exxpol Ex-101	Exact EX-201	Standard
Melt Index	50	110	55
Density, g/cm^3	0.923	0.923	0.926
Spiral Flow, In.	27.50	42.75	30.75
Tensile Str., psi			
Yield	1750	2000	2330
Break	1140	1110	1075
Elongation, %			
Yield	25	21	21
Break	275	73	77
Tensile Impact, ft-lb/in	13.4	6.8	9.4
Notched Izod Impact	NB	NB	NB
Total Energy Impact, in-lb	107	32	37
Flex Modulus, kpsl	52.6	68.7	66.5
Shrinkage, %	2.0	2.2	2.2

Table 1.21 Comparison of Metallocene Based Polyethylene Processes

S. No.	Process type	Company	MI range (g/10 min)	Density range (g/cm^3)	Nature of comonomer (%)	Reference
1.	Solution	Dow	0.5 to 30	0.880 to 0.950	octene (0 to 20%)	1
2.	Solution	Exxon	1 to 100	0.865 to 0.940	propylene, butene, hexene	2
3.	Gas phase	Mobil	1	0.918	hexene	3
4.	Gas phase	BP chemicals	2.3	0.916	hexene	4

(1) Sue Royse, *European Chemical News*, **60**, 13 Sep 1993, p35 (2) *European Chemical News*, **60**, 20 Sep 1993, p29 (3) Jan H. Schut, *Plastics Technology*, **39**, Jul 1993, p38 (4) Andrew Wood, and Gregory D. L. Morris, *Chemical Week*, **153**, Sep 1993, p18

Table 1.22 Properties of Gas phase LLDPE (Hexene-1 Comonomer) Using Supported Metallocenes

S. No.	Property	BP Chemicals[a]	Mobil[b]	Mobils standard hexene Ziegler-Natta
1.	Density g/cc	0.916	0.91	0.918
2.	Melt index	2.3	1	1
3.	MFR, g/10min	-	18	28
4.	Melt Point, °C	-	150.56	160.56
5.	Dart drop,g	900	>800	180
6.	Tear Strength g/mil			
	Machine direction	357	370	350
	Transverse direction	473	490	750
7.	Extractables, %	0.8	0.6	3.5
8.	Haze, %	-	5.7	18

[a] Angrew Wood and Gregory D L Morris, *Chemical Week*, **153**, Sep. 29 1993, p18 [b] *Plastics Technology*, **39**, July 1993, p38

The typical physical properties of modified isotactic and syndiotactic poly(propylene) are shown in Table 1.23 and compared with isotactic poly(propylene) prepared with Ti-Al catalysts.

The metallocene based catalysts have enabled the first ever practical synthesis of syndiotactic polystyrene, a polymer structure inaccessible by synthesis till 1989. Syndiotactic polystyrene possesses a high melting point (265°C), is crystalline and has an acceptable crystallization rate for commercial applications. Idemitsu and Dow have announced the first commercial plant for syndiotactic polystyrene within the next few years. Syndiotactic polystyrene has properties similar to many high cost engineering polymers, such as high heat, chemical and steam/water resistance, and may form components of high performance alloys[110].

Metallocenes are well suited to produce new qualities of polyolefins with easily recyclable nature which will minimize environmental pollution[111]. Development of metallocene catalysts, or widely speaking homogeneous catalysts may be a dominant force through the 1990s in the polyolefin industries[111].

Table 1.23 Physical Properties of Syndiotactic and Modified Isotactic Polypropylene Prepared using Metallocene Catalysts

Test	Syndiotactic PP	Modified Isotactic PP	Hostalen R1060 F
MFI 230/5 (g/10 min)	21	16	14
Modulus of elasticity 3 Pt Bending (N/mm^2)	600	1160	1480
Hardness, H 132/30 (N/mm^2)	40	-	75
Notched Impact Strength	17.5	-	7.6
Vicat Softening Point, °C	132	133	151
Density, (g/cm^3)	0.885	0.899	0.904

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CHAPTER 2

OBJECTIVES OF THE PRESENT INVESTIGATION

2.1 Objective in undertaking the present work

Ever since the discovery of homogeneous bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2)-alkylaluminum catalyst system for ethylene polymerization, homogeneous Ziegler-Natta catalysts have evinced interest for a variety of fundamental and applied reasons[1]. Recent discoveries in the area of homogeneous, highly active and stereospecific metallocene-aluminoxane catalysts[2] has stimulated renewed commercial and academic interest in these catalysts[3]. This is evidenced by the accumulation of large a volume of patented and published literature during the last 15 years.

Any hydrocarbyl aluminum compound on controlled reaction with water forms an aluminoxane. The most commonly used alkylaluminums for the synthesis of aluminoxanes are triisobutylaluminum (TIBAL), triethylaluminum (TEAL) and trimethylaluminum (TMA). Of the various aluminoxanes, methylaluminoxane (MAO) requires the greatest degree of control in its preparation because of the extreme reactivity of TMA with water. MAO is the most preferred aluminoxane for olefin polymerization.

The present investigation was undertaken with a view to understand some of the features of the MAO based homogeneous Ziegler-Natta catalysts on ethylene polymerization.

a) The reaction between water and alkylaluminums, unless properly controlled is highly exothermic, accompanied by flames and generates oxides of aluminum. MAO is generally prepared by controlled hydrolysis of TMA with water or hydrated salts at temperatures ranging between -80°C and 80°C. MAO thus synthesized appears to exist as an adduct with three molecules of TMA which even after distillation in presence of cumene or complexation with tetrahydrofuran retains one molecule of strongly associated TMA[4]. The precise structure of MAO remains ambiguous. On the basis of spectroscopic studies Sinn and coworkers postulated that MAO is a mixture of linear and cyclic oligomers of $[Al(Me)O]_n$ units ($n = 5\text{-}30$) depending upon the method of synthesis[5]. Recently, on the basis of X-ray crystallographic evidences of tert-butylaluminoxane Mason *et al.* proposed that MAO and related aluminoxanes have cluster type structures analogous to those found for the iminoalanes in which the aluminum centers are tetra-coordinate[6]. The degree of oligomerization, methyl to aluminum molar ratio, and the amount of free or complexed TMA to MAO are expected to vary depending on the reaction conditions like nature of water source, temperature, water to alkylaluminum ratio, and concentration of alkylaluminum employed during synthesis. The properties of MAO will also be affected by the process of recovery of MAO from the reaction mixture.

In spite of the large volume of published and patented literature on synthesis of MAO, details such as degree of oligomerization, methyl to aluminum molar ratio and the amount of free or complexed TMA (to MAO) are not routinely available. Hence, it is difficult to relate the polymerization behavior of a given MAO reported in the literature with its properties. Additionally, effect of free TMA on polymerization of ethylene using metallocene-MAO catalyst system has not been well studied so far.

b) Sterically hindered aryloxy derivatives of alkylaluminums have been shown to polymerize propylene and isoprene using β-$TiCl_3$ catalyst[7]. TMA on reaction with sterically hindered phenol like butylated hydroxy toluene gives a compound $AlMe(BHT)_2$, which is monomeric in nature and bears a similarity to the structure of the repeated unit of oligomeric MAO[8]. The use of $AlMe(BHT)_2$ as a cocatalyst component along with metallocenes for the polymerization of ethylene has not been reported so far.

One of the objectives of the present investigation is to synthesize MAO under different reaction conditions and characterize the synthesized MAO for methyl to aluminum molar ratio, molecular weight and % of TMA. It is also proposed to relate the catalytic effect of the MAO with its properties.

The other objective of the present investigation is to study the effect of added TMA to MAO, and reaction conditions like temperature, Al/Zr ratio, concentration of Cp_2ZrCl_2 and nature of aluminoxane on polymerization of ethylene using Cp_2ZrCl_2 catalyst. Finally the effect of $AlMe(BHT)_2$ as a cocatalyst on polymerization of ethylene using Cp_2ZrCl_2 as catalyst will be explored.

2.2 Approaches

2.2.1 Synthesis of MAO and its characterization and the study of ethylene polymerization using synthesized MAO

2.2.1.1 A crystal water method for the synthesis of MAO in toluene using different water sources and reaction conditions will be studied.

$$Al(CH_3)_3 \xrightarrow[\text{Hydrated salt}]{\text{Partial hydrolysis}} MAO$$

2.2.1.2 MAO will be characterized by ^{1}H-NMR, methyl to aluminum molar ratio and cryoscopic molecular weight.

2.2.1.3 Polymerization of ethylene using synthesized MAO as cocatalyst and Cp_2ZrCl_2 as catalyst in toluene at one atmospheric ethylene pressure will be investigated.

2.2.2 Studies of ethylene polymerization at one atmosphere ethylene pressure

2.2.2.1 Polymerization of ethylene will be studied as a function of reaction conditions such as [Al], [Zr], [Al]/[Zr] and temperature using Cp_2ZrCl_2-MAO catalyst system in toluene.

2.2.2.2 The effect of added TMA to MAO will be examined.

2.2.2.3 Polymerization of ethylene will be studied as a function of reaction conditions such as [Al], [Zr], [Al]/[Zr] and temperature using Cp_2ZrCl_2-tetraisobutyldialuminoxane catalyst.

2.2.2.4 Polymerization of ethylene will be explored in presence of $AlMe(BHT)_2$ to the Cp_2ZrCl_2-TMA catalyst system in toluene at 70°C.

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CHAPTER 3

SYNTHESIS, CHARACTERIZATION AND CATALYTIC STUDIES OF METHYLALUMINOXANE AND AlMe(BHT)$_2$

3.1 Introduction

Discovery of homogeneous bis(cyclopentadienyl)titanium (IV) dichloride-alkylaluminum catalyst system by Breslow and coworkers for ethylene polymerization kindled considerable interest in the area of soluble catalyst for olefin polymerization[1]. However, for over twenty years homogeneous catalyst did not attract wide spread interest because of the poor catalyst activity, short kinetic life time and lack of stereospecificity. To overcome these disadvantages researchers tried to modify these catalysts (Ti or Zr based catalysts), cocatalysts (alkylaluminums) etc.,

The accidental observation of increase in catalytic activity in presence of moisture for the polymerization of ethylene using alkylaluminum cocatalysts lead to the discovery of methylaluminoxane (MAO), a cocatalyst[2]. This fact has stimulated renewed commercial and scientific interest in homogeneous catalysts. MAO is prepared by controlled and partial hydrolysis of trimethylaluminum (TMA). The typical structural element of MAO is an oxygen atom joining two aluminum atoms that still bear a methyl group. MAO is found to be oligomeric in nature and the preferred MAO for olefin polymerization contains about 4 to 30 of the repeating units: [-O-AlMe-]. The precise structure of MAO is, however, still shrouded in mystery.

There are several methods available for the synthesis of MAO, among which the crystal water method is widely used. Different methods for the synthesis and characterization of MAO have been discussed in detail in Chapter I. Although MAO has been extensively used in olefin polymerization, and is even commercially available, very little has been reported in the literature regarding reaction variables associated with its synthesis, their effect on MAO properties and their effect on polymerization reactions.

Jeffery and Mole demonstrated that alkylaluminum reagents could be modified readily by reaction with phenols[3]. This approach has subsequently been subject of considerable work in a number of laboratories[4,5]. Simple phenols give compounds that are bridged through the oxygen atoms of the resulting phenoxide group whereas, sterically hindered phenols give products that are monomeric in nature[6]. These monomeric species, usually synthesized from 2,6-di-tert-butyl substituted phenols, have found application in organic synthesis[7-8] and the preparation of a new generation of Ziegler-Natta catalysts that display the unusual combination of high activity and high stereospecificity in the polymerization of propylene[9-12].

Though sterically hindered aryloxy derivatives of alkylaluminum have been shown to polymerize propylene and isoprene using β-$TiCl_3$ catalyst, however, these compounds have not been studied as cocatalysts for ethylene polymerization using metallocene catalysts.

In this chapter the synthesis and characterization of MAO and $AlMe(BHT)_2$ (a sterically hindered aryloxy derivative of trimethylaluminum) are discussed. Also ethylene polymerization studies using the synthesized MAO as cocatalyst and Cp_2ZrCl_2 as catalyst are discussed. Ethylene polymerization studies using the synthesized $AlMe(BHT)_2$ as cocatalyst and Cp_2ZrCl_2 as catalyst are discussed in chapter IV.

3.2 Experimental Procedures

All manipulations involving air sensitive compounds were performed either inside a Labconco Model 50004 inert atmosphere glove box continuously purged with high purity N_2 (<5 ppm moisture) generated using N_2 generator (Spantech, Model NG 300-1, England) or under a positive pressure of high purity N_2 (<5 ppm moisture, <5 ppm oxygen) or using standard bench top inert atmosphere techniques[13].

3.2.1 Materials

TMA (Schering-A.G., Germany) was used as received. Sulphur free benzene and toluene (Loba-AR, Bombay) were purified by refluxing over sodium metal. After refluxing for 48 h over sodium wire the solvents were distilled out and once again refluxed over freshly added sodium wire for 24 h under dry N_2 atmosphere. The solvents were distilled just prior to use under N_2 atmosphere. Butylated hydroxy toluene (BHT) (2,6-di-tert-butyl-4-methyl phenol) (Loba, Bombay) recrystallized in n-hexane was used for the synthesis of sterically hindered aryloxy derivative of TMA, viz., $AlMe(BHT)_2$. $Al_2(SO_4)_3$ 14.5 H_2O (Loba, Bombay) was used as such for the synthesis of MAO. Polymerization grade ethylene was obtained from the Maharashtra Gas Cracker Complex of Indian Petrochemical Corporation Limited at Nagothane, India. It had a moisture content of <4 ppm (Shaw Model SHA-TR moisture analyzer) and oxygen content of <3 ppm (Braun Oxygen Analyzer). Freshly distilled methanol was used for quenching the polymerization and for further precipitation and washing of the poly(ethylene). Decalin (Aldrich, USA) was used as received for the determination of the intrinsic viscosity of the poly(ethylene). EDTA (SD-Fine Chemicals, Bombay), $ZnSO_4.7H_2O$ (SD-Fine Chemicals, Bombay) Dithizone indicator (Loba, Bombay) $KAl(SO_4)_2$ $12H_2O$ (SD-Fine Chemicals, Bombay), acetone (SD-Fine Chemicals, Bombay) and 1-heptanol (Loba, Bombay) were used as received.

3.2.2 Synthesis of methylaluminoxane

TMA (8.35 g, 0.1185 mol) was placed in a 100 mL conical flask equipped with a teflon rotaflow stopcock side arm under a positive pressure of N_2. TMA was diluted with 35 mL dry toluene. In a four necked 250 mL round bottomed flask equipped with a teflon magnetic needle (the flask was dried overnight at 120°C and cooled under N_2 atmosphere) 11.35 g of $Al_2(SO_4)_3$ 14.5. H_2O was placed and was dispersed in 60 mL of dry toluene. The two necks of the flask were connected to N_2 inlet and outlet respectively. The third neck was fitted with a rubber septum and the fourth neck with a thermowell. Both the TMA containing flask and $Al_2(SO_4)_3$ 14.5 H_2O containing flask were cooled to -10°C using ice+salt mixture. Then toluene solution of TMA was added in a thin stream into the $Al_2(SO_4)_3$ 14.5 H_2O containing flask under a positive pressure of N_2 using a cannula. The vigorousness of the reaction was noticed by the evolution of methane gas. After the complete addition of toluene solution of TMA the reaction mixture was slowly heated to 0°C and then to 30°C by removing the ice+salt mixture (No external heating is required). The temperature of the reaction was measured throughout the reaction. After 4 h of reaction at 30°C, temperature was increased to 50°C for six more hours. Methyl/aluminum molar ratio was determined periodically during the reaction.

After the completion of 10 h reaction time the reaction mixture was filtered into a two necked flask under a positive pressure of N_2. The filtrate was analyzed for methyl/aluminum molar ratio, and % TMA. This filtrate MAO will hereafter be designated as Fraction A.

Around 30 mL of Fraction A was taken into a two necked weighed round bottomed flask equipped with a teflon magnetic needle. The volatiles were distilled off under reduced pressure (10 mm Hg) at room temperature (30°C) until a white solid appeared. This solid was further dried for about 20 minutes under the same conditions. The free flowing solid (0.87 g, yield = 40%) was then dissolved in 6.11 g of dry benzene. This MAO in benzene will hereafter be mentioned as Fraction B. Fraction B was analyzed for methyl/aluminum molar ratio, % TMA and molecular weight.

3.2.3 Characterization of MAO

3.2.3.1 [Me]/[Al] molar ratio

Methyl content: Methyl content in MAO was determined by hydrolyzing the compound in a mixture of 1-heptanol (50 mL) and dil. H_2SO_4 (2N H_2SO_4, 30 mL) in a two necked jacketed reactor. One of the necks of the reactor was connected to the gas burette where the evolved methane gas could be measured and the other neck was fitted with a rubber septum. The gas burette had an outer jacket. Water at 30°C was circulated through the outer jacket of the reactor and the gas burette. The inner tube of the gas burette and the side reservoir (to maintain the atmospheric pressure) are filled with silicone oil. By adjusting the side reservoir initial reading in the gas burette was measured at atmospheric pressure and known temperature (temperature of the reactor and gas burette were maintained by circulating water at 30°C). A 0.5 mL MAO solution in toluene (Fraction A) was injected into the reactor through the rubber septum using a 1 mL hypodermic syringe. The evolved methane gas collected in the gas burette was measured as the difference between the final (after decomposition of the compound) and initial (before decomposition of the compound) readings of the burette. Moles of methane gas evolved were calculated after correcting the volume of the evolved methane gas to S.T.P. The assembly for the methyl content estimation is shown in Figure 3.1. A typical calculation is shown below.

Initial burette reading = 24.0
Final burette reading = 32.3

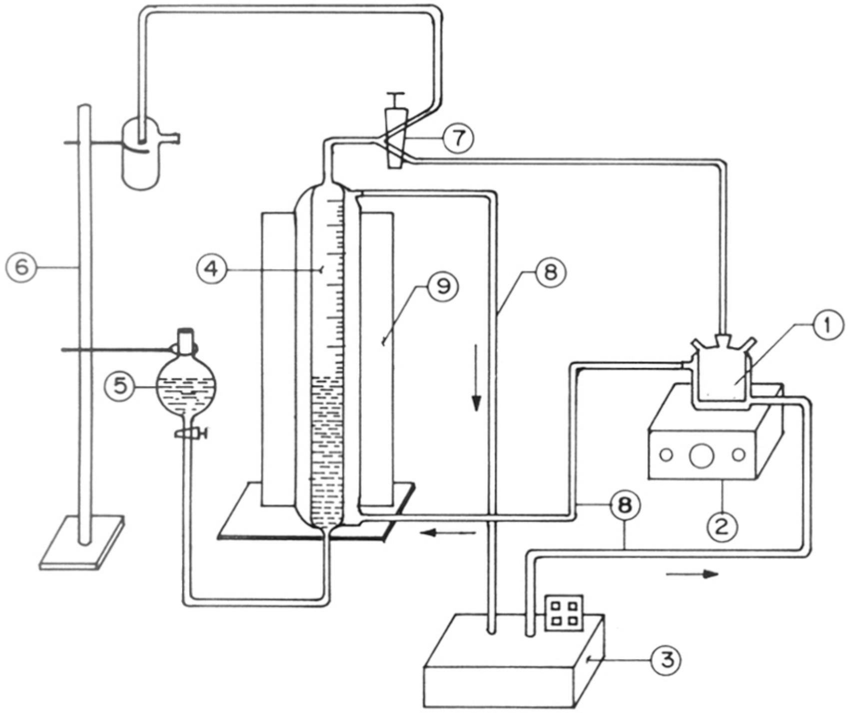
Total volume of methane evolved at 30°C = 8.3 mL

Total volume of methane evolved at S.T.P. = $\frac{8.3 \times 273}{303} = 7.5$ mL

$$\text{Moles of methane evolved} = \frac{\text{mL of methane evolved at S.T.P.}}{\text{The volume of 1 mole of methane at S.T.P. in mL}}$$

$$= \frac{7.5}{22414} = 3.32 \times 10^{-4} \text{ mol}$$

Aluminum content: Aluminum content in MAO was determined by EDTA back titration method, employing $KAl(SO_4)_2\ 12.H_20$ as standard and dithizone as indicator at a pH = 5. Ammonium acetate and acetic acid were employed for the preparation of buffer of pH 5. MAO solution 0.5 mL (Fraction A) as used for the determination of methyl content was used for the determination of aluminum content. The MAO was hydrolyzed using dil.H_2SO_4 (around 10 to 15 mL) in a standard 50 mL volumetric flask. The hydrolyzed compound



① GLASS REACTOR	⑥ IRON STAND
② MAGNETIC STIRRER	⑦ THREE WAY STOPCOCK
③ JULABO WATER BATH	⑧ POLYETHYLENE WATER TUBING
④ GAS BURETTE (100 mL CAPACITY)	⑨ WOODEN STAND TO SUPPORT GAS BURETTE
⑤ SEPARATING FUNNEL WITH SILICON OIL	

Fig. 3.1 Methane gas estimation setup

was made upto the mark in the volumetric flask by adding deionized water. From this solution 5 mL was taken into a 100 mL conical flask with a pipette and subsequently 10 mL EDTA (0.01 M) and 10 mL buffer (pH = 5) were added. Approximately 10 mL of ethanol was added finally in to the conical flask using a measuring jar to note the end point clearly. After adding dithizone indicator (in acetone) the solution was titrated against $ZnSO_4\ 7H_2O$ (0.01 M) to estimate the uncomplexed EDTA. At the end point color changes from violet to pink. The EDTA complexed to aluminum was calculated by subtracting the volume of zinc sulphate solution consumed from the total EDTA. The actual amount of aluminum present in the solution was calculated by equating with the standard aluminum sulphate solution. A typical calculation is shown below.

For 5 mL unknown solution the amount of $ZnSO_4$ consumed = 5.1 mL

EDTA complexed to aluminum = Total EDTA - Volume of $ZnSO_4$ consumed

$$= 10 - 5.1 = 4.9 \text{ mL}$$

2.3 mL EDTA corresponds to 0.0006787 g Al (Standard equation)

4.9 mL EDTA corresponds to

$$= \frac{0.0006787 \times 4.90}{2.3} = 0.0014472 \text{ g of Al}$$

For 5 mL unknown solution 0.0014472 g of Al is present

For 50 mL unknown solution

$$= \frac{50 \times 0.0014472}{5} = 0.014472 \text{ g of Al}$$

Therefore moles of Al present in 0.5 mL of original solution of Fraction A

$$= \frac{0.014472}{27} = 2.01 \times 10^{-4} \text{ moles}$$

Methyl/aluminum molar ratio was calculated from the volume of methane gas evolved to the aluminum present in the same amount of MAO. A representative calculation is shown below.

$$\text{Methyl/aluminum molar ratio} = \frac{\text{Moles of methane evolved for 0.5 mL of Fraction A}}{\text{Moles of aluminum present in 0.5 mL of Fraction A}}$$

$$\text{Methyl/aluminum molar ratio} = \frac{3.32 \times 10^{-4}}{2.01 \times 10^{-4}} = 1.65$$

3.2.3.2 % TMA in MAO (it is calculated by neglecting the chain ends of MAO (i.e. -O-Al($(CH_3)_2$) if the compound is linear)

The % TMA present in MAO was calculated by using both methyl/aluminum molar ratio and ^{1}H NMR techniques.

a) Using Me/Al molar ratio: The following equation was employed to determine the % TMA in MAO.

$$\frac{\text{Total Methyl content (moles)}}{\text{Total Aluminum content (moles)}} = \frac{a + 3b}{a + b}$$

Where "a" corresponds to MAO and "b" corresponds to TMA. From the repeating unit of MAO it is noted that MAO contains "a" moles of methyl and "a" moles aluminum. TMA contains "3b" moles of methyl and "b" moles of aluminum. Therefore total methyl content in MAO (MAO + TMA) is "a + 3b" and total aluminum content is "a + b". Using the methyl/aluminum molar ratio determined using analytical techniques mentioned above one can calculate the value of "b" i.e., moles of TMA present in MAO. The percentage of TMA present in MAO was calculated by substituting the value of "b" in the following equation.

$$\% \text{ TMA} = \frac{b}{(a+b)} \times 100$$

A typical calculation is shown below.

$$\frac{\text{Total Methyl content (moles)}}{\text{Total Aluminum content (moles)}} = \frac{a + 3b}{a + b} = 1.65$$

$$1.65a + 1.65b = a + 3b$$

$$0.65\ a = 1.35\ b$$

$$a/b = 1.35/0.65 = 2.0769$$

Moles of MAO (a) = 2.0769 Moles of TMA (b) = 1

$$\% \text{ TMA} = \frac{b}{(a+b)} \times 100 = \frac{1}{3.0769} \times 100 = 32.5$$

b) Using ^{1}H NMR: ^{1}H NMR of MAO was taken in toluene-d_8 on a Bruker AC-200 spectrometer (Figure 3.2). Resconi *et al.* have calculated the % of TMA present in MAO using ^{1}H NMR technique[14]. ^{1}H NMR of MAO as reported gave a broad peak centered in the region of -0.35 ppm. A sharp signal was observed as reported for TMA at -0.20 ppm. From the integrations of the MAO broad peak and TMA sharp peak the % TMA in MAO was calculated.

The % TMA calculated using methyl/aluminum molar ratio was in agreement with the values obtained using the ^{1}H NMR.

3.2.3.3 Molecular weight of MAO

The molecular weight of MAO was determined by cryoscopy technique using benzene as solvent. The whole experiment was conducted in N_2 atmosphere. Beckmann thermometer having 0 at top was used for measuring the depression in freezing point of the MAO solution. Benzene 10 mL (weighed) was placed into the cryoscopy apparatus (Figure 3.3). The apparatus was then immersed in a thermostat at a temperature of 5°C. Under a positive pressure of N_2 the

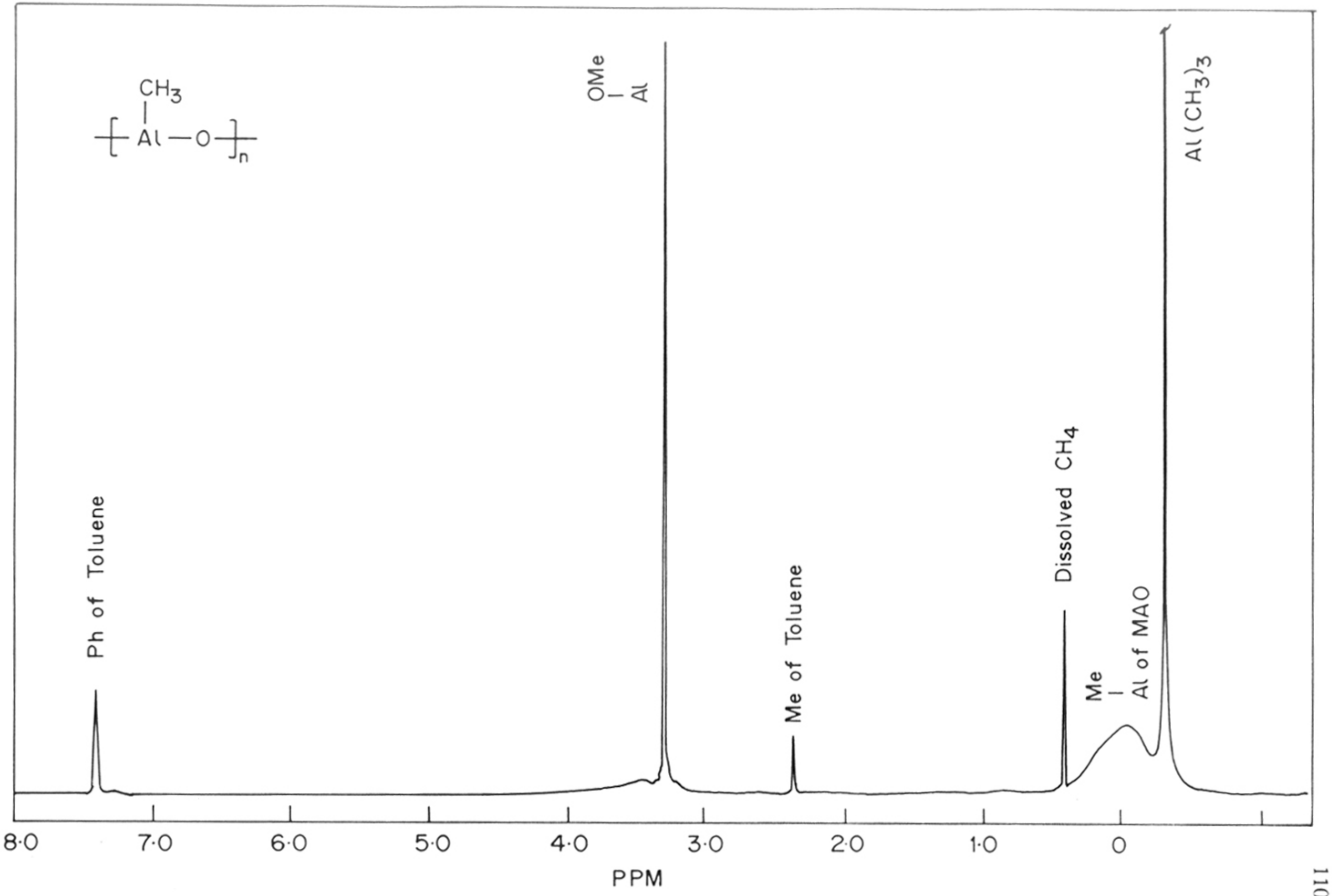
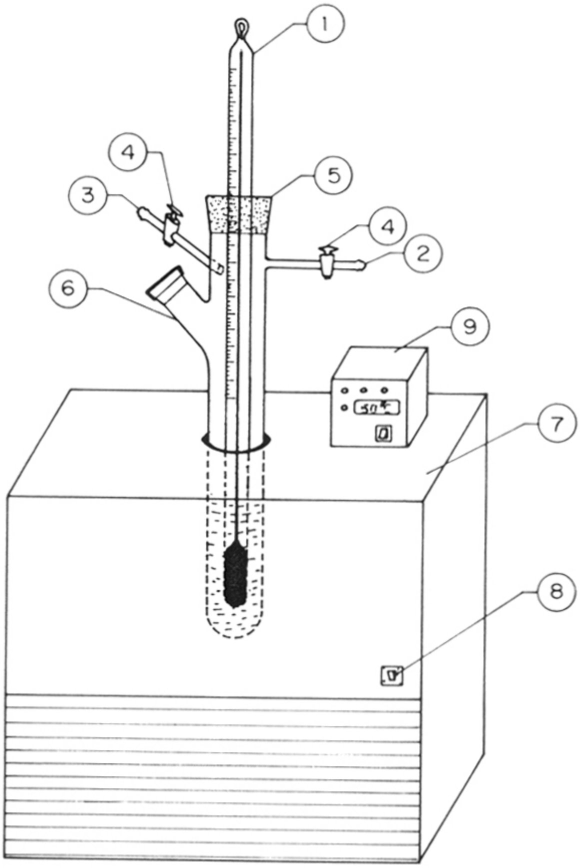


Fig. 3.2 200 MHz ^{1}H-NMR spectrum of MAO in toluene-d_8



1. BECKMANN THERMOMETER
2. N_2 INLET
3. N_2 OUTLET
4. 2-WAY STOPCOCKS
5. RUBBER CORK WITH A HOLE
6. SIDE ARM WITH A RUBBER SEPTUM
7. JULABO LOW TEMPERATURE BATH
8. COOLING SWITCH
9. TEMPERATURE CONTROLLER

Fig. 3.3 Cryoscopy apparatus for the molecular weight determination of air sensitive compounds under inert atmosphere

Beckmann thermometer (The mercury thread in the Beckmann was already set to 0 at 5°C and was kept in the refrigerator at 0°C until further use) was placed into the cryoscopy apparatus after removing the moisture present around the bulb of the thermometer (The moisture present around was removed by rinsing the thermometer with cooled benzene at 5°C. This rinsing of the thermometer was done 3 to 4 times using freshly cooled benzene each time to ensure the complete removal of moisture). Slowly the bath temperature was decreased upto 4.4°C. Then the Beckmann was disturbed manually until the freezing of the benzene started. Once freezing of the benzene started the mercury thread rose suddenly and reached a constant point. This was noted as the freezing point of benzene. The solid benzene was melted by increasing the temperature of the bath. After complete melting of the solid benzene into liquid state a known concentration of benzene solution of MAO (7 to 10 g/kg of the total solution) was placed into the cryoscopy apparatus. The freezing point of this solution was determined as before. The difference in the freezing points of benzene and the solution gave the depression in the freezing point. The molecular weight of the MAO was calculated from the equation.

$$\Delta T_f = K_f m$$

$$M = \frac{\text{Concentration of MAO}}{m}$$

where ΔT_f = depression in freezing point, K_f = cryoscopic constant for benzene, m = molar mass expressed in mol/kg, M = molecular weight of MAO (g/mol). The concentration of MAO solution is taken as g/kg.

A typical calculation is shown below.

Concentration of Fraction B of MAO III in benzene = 9.4419 g/kg

F.P. of benzene on Beckmann thermometer = 0.085

F.P. of solution on Beckmann thermometer = 0.145

Depression in F.P. = ΔT_f = 0.06

K_f for benzene = 5.12 mol/kg (which is constant)

$$m = \frac{\Delta T_f}{K_f} = \frac{0.06}{5.12} = 0.011787 \text{ kg/mol}$$

$$\text{Mol. Wt. of MAO (M)} = \frac{\text{Concentration}}{m} = \frac{9.4419}{0.11787} = 805 \text{ g/mol}$$

3.2.4 Synthesis of $AlMe(BHT)_2$

$AlMe(BHT)_2$ was prepared by reacting TMA with sterically hindered 2,6-di-tert-butyl-4-methyl phenol (Butylated hydroxy toluene, BHT) as per the literature procedure[6]. BHT (0.023 mol) was taken in a three necked 100 mL round bottomed flask which had been dried over night at 120°C and cooled under N_2. Toluene (30 mL) was added to BHT till it dissolved. Thereafter a toluene solution of TMA (0.09 mol) was added dropwise under a positive pressure of N_2. Vigorous gas evolution was observed. The reaction mixture was stirred for 12 h at 25 - 27°C. The solvent was distilled off under reduced pressure (10 mm Hg) at 30°C and the residual solid was washed with excess of n-hexane and dried under vacuum. The yield is 95%.

3.2.5 Characterization of AlMe(BHT)$_2$

The synthesized compound was characterized by melting point, methyl/aluminum molar ratio, ^{1}H NMR, and by molecular weight determination using mass spectroscopy and cryoscopy methods.

3.2.5.1 Melting point

Melting point of the compound was determined in a specially designed capillary (Figure 3.4). A small amount of compound was placed into the capillary inside an inert atmosphere box. Then the capillary was evacuated and sealed under vacuum. This sealed capillary containing the compound was used for the determination of the melting point. The compound showed a melting point of 165°C which matches with the reported value of 165°C for AlMe(BHT)$_2$[6].

3.2.5.2 Methyl/aluminum molar ratio

Methyl/aluminum molar ratio was determined according to the procedure given for MAO. The ratio was found to be one. If two methyl groups in TMA are replaced by sterically hindered phenoxy groups the methyl/aluminum molar ratio will be one. Therefore, the ratio is in agreement with the structure AlMe(BHT)$_2$.

3.2.5.3 ^{1}H NMR

^{1}H NMR of the compound was recorded in toluene-d$_8$ on a Bruker AC-200 spectrometer. The NMR sample was prepared inside the glove box to avoid the decomposition of the compound. The observed values were compared with the reported values for the compound AlMe(BHT)$_2$[6] (Table 3.1). The ^{1}H NMR spectrum of the synthesized compound is shown in Figure 3.5.

3.2.5.4 Molecular weight

Molecular weight of the synthesized compound was determined by using cryoscopy in benzene as well as by mass spectrometry.

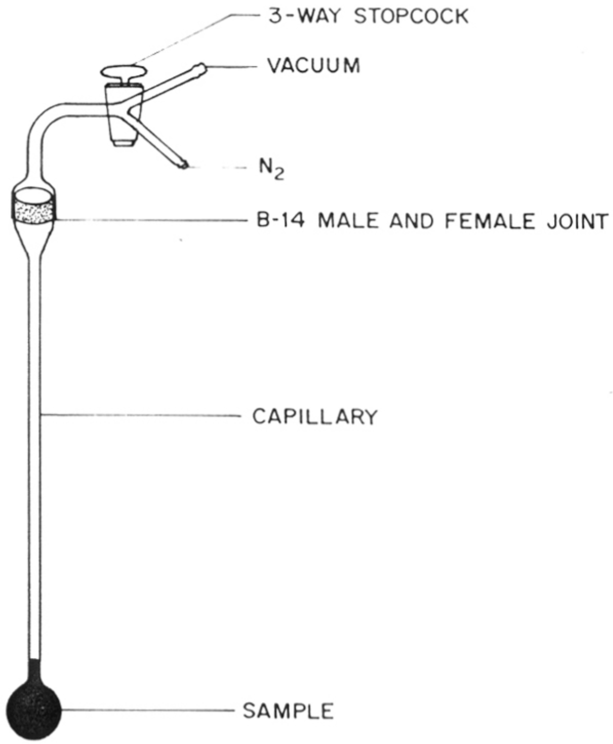


Fig. 3.4 Capillary for the determination of melting point of air sensitive compounds

Table 3.1 Comparative Data for ^{1}H NMR Values of Synthesized Compound with the Reported Values for the Compound AlMe(BHT)$_2$

Observed value (ppm)	reported value (ppm)	segment assigned
-0.23	-0.23	Al-CH_3
1.61	1.61	tert-butyl
2.35	2.35	Ph-CH_3
7.13	7.13	3,5-H of phenyl ring

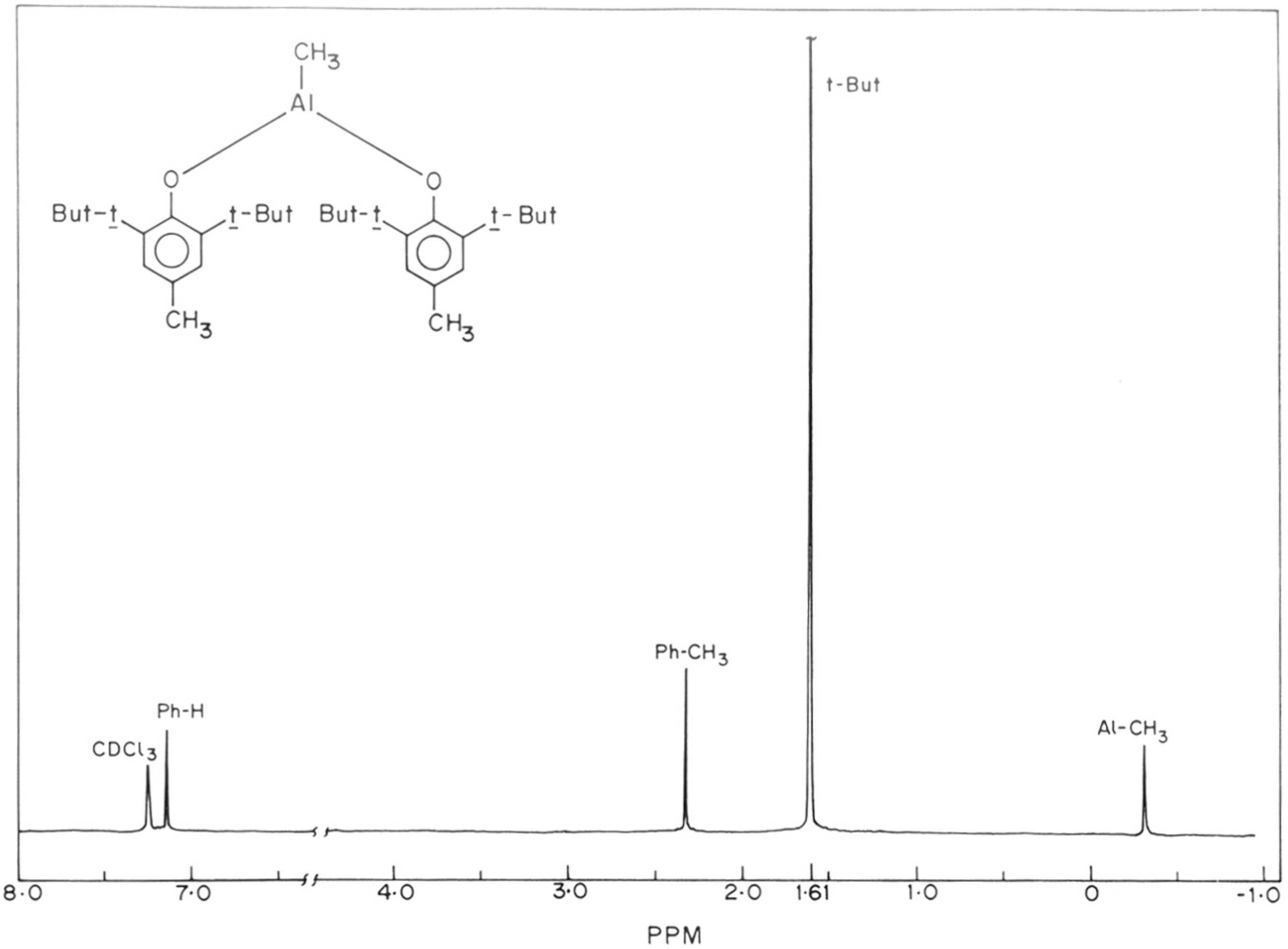
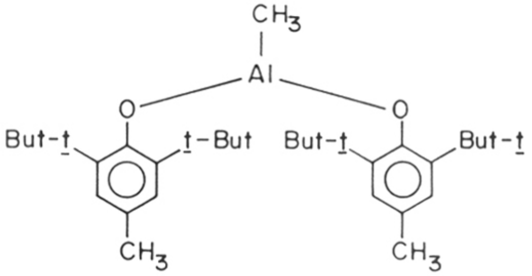


Fig. 3.5 200 MHz ^{1}H-NMR spectrum of AlMe(BHT)$_2$ in toluene-d$_8$

a) Cryoscopy: Cryoscopy of the compound was performed using the procedure given for the molecular weight determination of MAO in this chapter. The molecular weight of the compound was found to be 480 which is in agreement with the reported molecular structure for $AlMe(BHT)_2$[6].

b) Mass spectrometry: Mass spectrum of the synthesized compound was recorded using Finnigan MAT 1020B Mass spectrometer. The observed m/z values are 480 (M^+), 465 (M^+ - Me), 246 [Al(BHT)]. The molecular ion peak is matching with the expected M+ peak.

The above mentioned analytical data confirm the structure of the synthesized compound as $AlMe(BHT)_2$.



$AlMe(BHT)_2$

3.3 Results and Discussion

This section is divided into two parts for the sake of convenience.

3.3.1 Effect of reaction temperature and time on properties of MAO

Three samples of MAO were synthesized by employing different reaction conditions given below.

I. Reaction temperature 30°C and reaction time 6 h

II. Reaction temperature 30°C for 4 h and then temperature raised to 50°C for further 4 h

III. Reaction temperature 30°C for 4 h and then temperature raised to 50°C for further 6 h

TMA : H_2O mole ratio for all the three reactions were taken as 1:2 (TMA : H_2O = 0.143 : 0.282). The concentration of toluene solution of TMA (3.22 g Al/100 mL) was also the same in all the three reactions. The results of these experiments are shown in Table 3.2. The methyl/aluminum molar ratio versus time graph for all the three reactions are shown in Figure 3.6. Methyl/aluminum molar ratio versus molecular weight plot of the synthesized MAOs are shown in Figure 3.7.

In each MAO synthesis, two types of MAOs were isolated. One the filtrate from the reaction mixture (A), and the other, obtained by drying the filtrate MAO under vacuum and dissolving the resulting solid in benzene (B).

Upon increase in reaction time as well as temperature the methyl/aluminum molar ratio and % TMA decreased (Figure 3.6). According to Sinn and coworkers MAO forms an adduct with three molecules of TMA which even after distillation in the presence of cumene or complexation with tetrahydrofuran retains one molecule of strongly associated TMA[15]. The presence of residual TMA in MAO has also been detected by ^1H NMR[14] as well as GPC[16]. The average molecular weight of the MAO increased with increase in reaction time and temperature (Table 3.2). This can be attributed to the increase in the degree of oligomerization as a result of increase of extent of condensation reaction between water and TMA or increase of extent of hydrolysis of TMA.

A plot of methyl/aluminum molar ratio against average molecular weight of the MAOs is shown in Figure 3.7. As expected Fraction A shows higher methyl/aluminum molar ratio and higher content of TMA compared to Fraction B (Table 3.2).

Table 3.2 MAO Synthesis and Properties

	MAO I		MAO II		MAO III	
Synthetic conditions	TMA = 0.143 mol, $Al_2(SO_4)_3$ 14.5 H_2O = 0.282 mol (as water), TMA : H_2O = 1:2, [TMA] = 3.22 gAl/100 mL toluene, Addition of TMA at -10°C, Reaction temperature: 30°C for 6 h		TMA = 0.143 mol, $Al_2(SO_4)_3$ 14.5 H_2O = 0.282 mol (as water), TMA : H_2O = 1:2, [TMA] = 3.22 gAl/100 mL toluene, Addition of TMA at -10°C, Reaction temperature: 30°C for 4 h and then at 50°C for 4 h		TMA = 0.143 mol, $Al_2(SO_4)_3$ 14.5 H_2O = 0.282 mol (as water), TMA : H_2O = 1:2, [TMA] = 3.22 gAl/100 mL toluene, Addition of TMA at -10°C, Reaction temperature: 30°C for 4 h and then at 50°C for 6 h	
Time of reaction (min)	Methyl/aluminum (mol ratio)		Methyl/aluminum (mol ratio)		Methyl/aluminum (mol ratio)	
	Fraction A	Fraction B	Fraction A	Fraction B	Fraction A	Fraction B
90	2.40		2.45		2.42	
240	2.20		2.22		2.21	
360	2.07	1.63	2.01		2.10	
480	-		1.75	1.55	-	
600	-		-		1.65	1.50
TMA (mol%)	53.0	29.0	37.5	27.5	32.5	25.5
Cryoscopic molecular weight		420		590		805

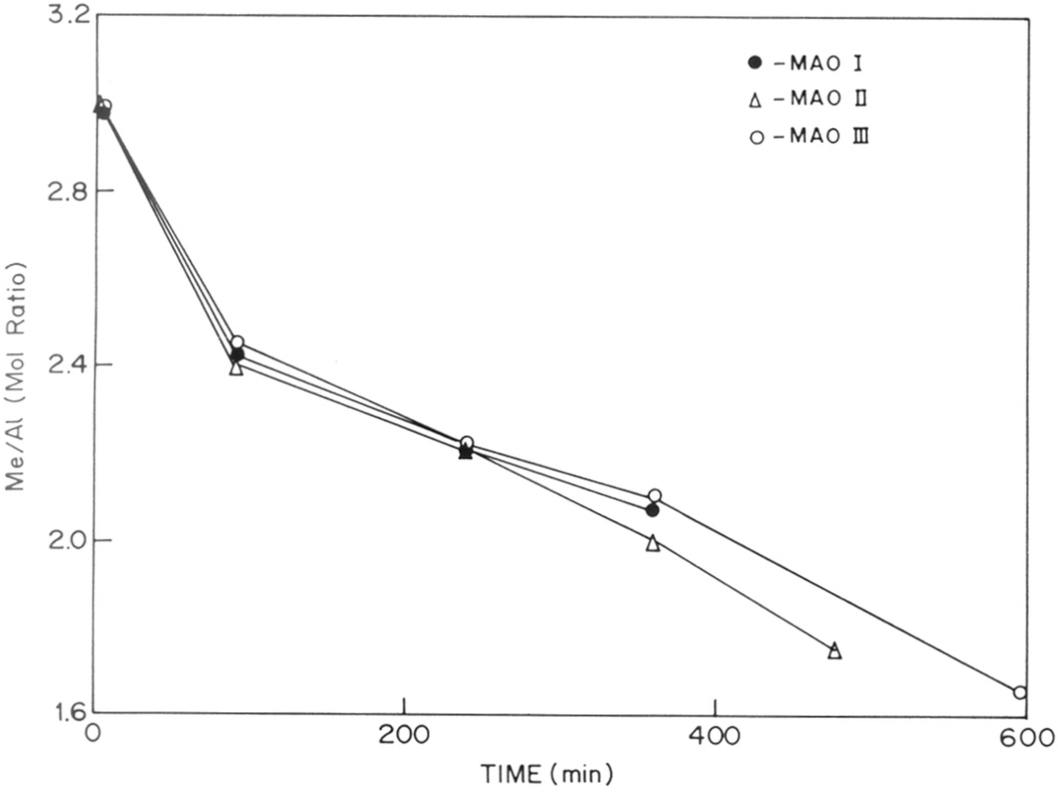


Fig. 3.6 Plot of methyl/aluminum (mol ratio) vs time (min) during the preparation of MAOs I, II and III

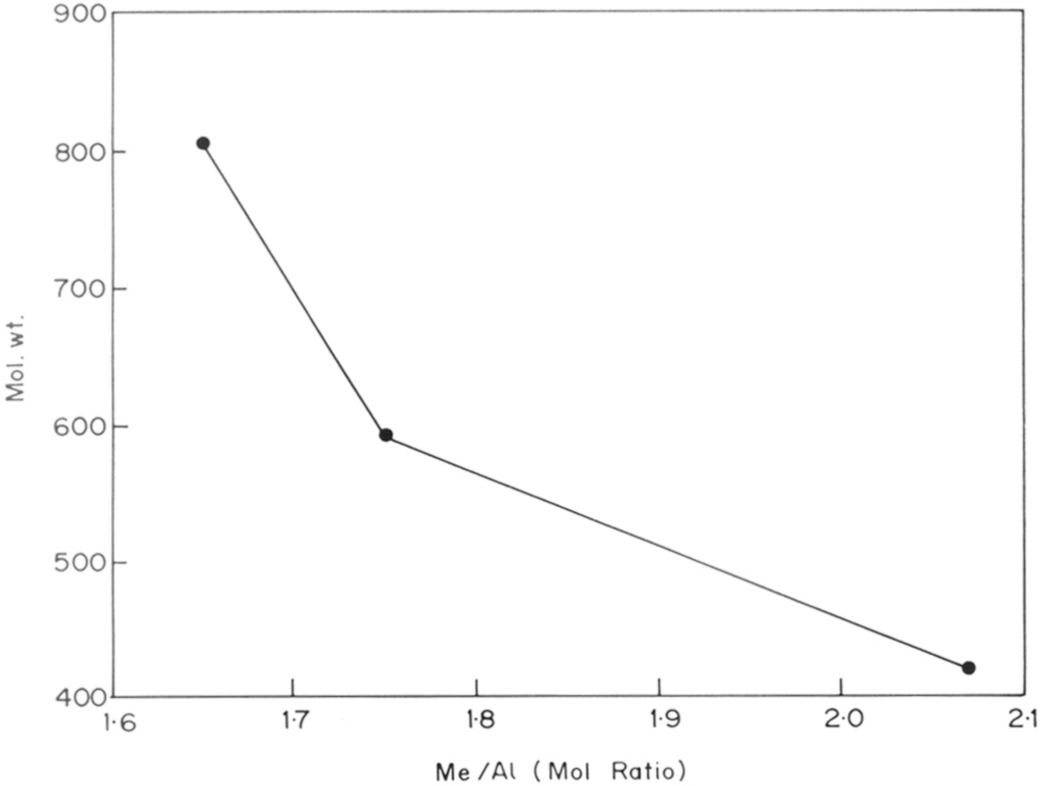


Fig. 3.7 Plot of molecular weight of MAO vs methyl/aluminum (mol ratio)

3.3.2 Effect of methyl/aluminum molar ratio, mol% TMA and average molecular weight of MAOs on ethylene polymerization

Ethylene polymerization was conducted using Cp_2ZrCl_2 catalyst in combination with MAOs (both Fraction A and Fraction B from reactions I, II and III) at 70°C and one atmospheric pressure in toluene. All the ethylene polymerizations were conducted at [Al] concentration of 8.8×10^{-2} mol/L, [Zr] concentration of 8.8×10^{-7} mol/L, and [Al]/[Zr] of 1,00,000. The results are shown in Table 3.3 and in Figure 3.8.

For Fraction A (in case of II and III) catalyst activity for ethylene polymerization was found to be higher when compared to Fraction B from the corresponding reaction (Table 3.3). This is due to the presence of high TMA content in these MAOs. It has been reported that in the case of MAO cocatalyzed polymerizations the actual cocatalyst is the residual TMA present along with MAO. But when different MAOs I, II and III (both Fraction A and B) are compared for their catalyst activity, it is observed that MAO III with a methyl/aluminum molar ratio of 1.65 and 32.5% TMA content shows the highest catalytic activity.

The Rp versus time for ethylene polymerizations showed a decay type curve for MAO III (Fraction A and B) cocatalyzed polymerizations (Figure 3.8). For MAO I cocatalyzed polymerizations the Rp versus time curve is an initial build up type which subsequently attains steady state. For MAO II it is observed that the Rp versus time curve is a moderate decay type curve. It may be recalled that TMA cocatalyzed ethylene polymerization shows a kinetic profile of build up type. In the case of commercial MAO (Schering-A.G., Germany) cocatalyzed ethylene polymerization a decay type kinetic profile was observed. (These studies are discussed in chapter IV). MAO I behaves more like TMA cocatalyst which is due to its lower molecular weight and high content of TMA. Therefore it can be concluded that a minimum molecular weight is necessary for MAO to show high rates of polymerization. MAO III having a molecular weight of 805, methyl/aluminum molar ratio of 1.65 and a 32.5% TMA content shows a decay type kinetic profile similar to that reported for commercial MAO

Table 3.3 Ethylene Polymerization Studies Using Cp_2ZrCl_2-Synthesized MAOs[a]

MAO parameters					Polymerization		
Expt. No.	Fraction	Me/Al (mol ratio)	TMA (mol%)	Cryoscopic Mol. Wt.	Activity (Kg-PE/g-Zr.h.atm)	Initial Rp.10^{-4} (M.Sec^{-1})	$[\eta]^b$ (dL/g)
I	A	2.07	53		280	0.6	1.04
I	B	1.63	29	420	330	0.9	1.50
II	A	1.75	37.5		785	2.6	2.9
II	B	1.55	27.5	590	719	2.3	3.0
III	A	1.65	32.5		1040	5.4	3.2
III	B	1.50	25.5	805	860	3.4	3.1
MAO	Commercial	1.60	30.0	850	1000	4.0	1.7

[a] Polymerization conditions: [Al] = 8.8 x 10^{-2} mol/L, [Al]/[Zr] = 100000, Temperature = 70°C, Toluene = 30 mL, [b] intrinsic viscosity determined at 135°C in decalin

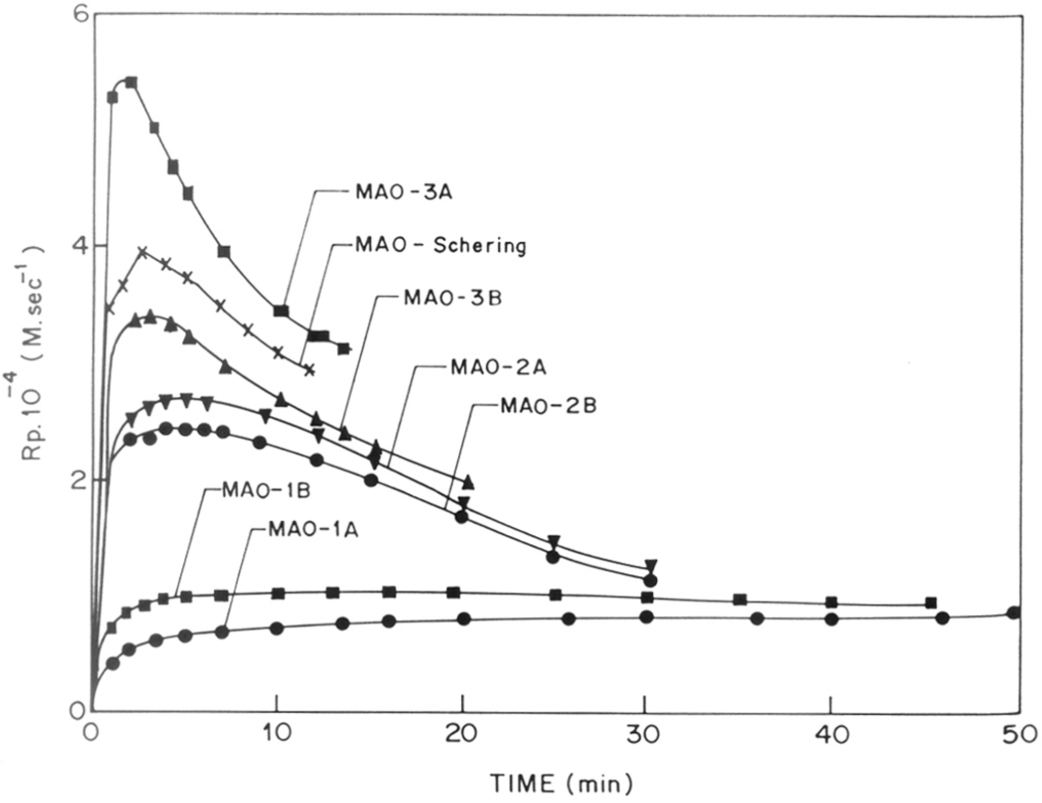


Fig. 3.8 Polymerization of ethylene using Cp_2ZrCl_2-MAO - Kinetic profile

cocatalyzed ethylene polymerizations. MAO II with a molecular weight of 590, methyl/aluminum molar ratio of 1.75 and 37.5 mol% TMA content shows an intermediate behavior between the two extreme cases. These observations are in agreement with earlier reports concerning the catalyst activity of bis(cyclopentadienyl)dimethyl titanium(IV) which increased with an increase in the degree of oligomerization of MAO, for ethylene polymerization[17,18]. It is also generally recognized that in order to obtain a good catalyst activity, the cocatalyst MAO must have a minimum critical degree of oligomerization[19].

The intrinsic viscosity of the poly(ethylene)s obtained using Fraction A and Fraction B cocatalyzed polymerizations (in case of MAOs II and III) (Table 3.3) is essentially similar. Intrinsic viscosity of poly(ethylene) obtained using MAO III is found to be higher. This is due to the presence of lower % TMA. TMA is a well known chain transfer agent in olefin polymerization. The properties of the two MAO's (MAO III and commercial MAO) such as molecular weight, methyl/aluminum molar ratio, % TMA are quite comparable. The intrinsic viscosity of poly(ethylene) obtained using Cp_2ZrCl_2-commercial MAO catalyst was 1.7 as compared 3.2 in the case of Cp_2ZrCl_2-MAO III. Activity of the catalyst system remains unaltered.

3.4 Conclusions

These results clearly suggest that in order to get high catalytic activity with high initial Rp and high molecular weight poly(ethylene), MAO molecular weight should be higher than a critical minimum which is around 800, have a methyl/aluminum molar ratio of around 1.6 and TMA content of approximately 30%. These results have implications on the choice of method for the synthesis of a MAO and its use in the polymerization of olefins.

3.5 References

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CHAPTER 4

POLYMERIZATION OF ETHYLENE USING GROUP IV METALLOCENE BASED HOMOGENEOUS CATALYSTS

4.1 Introduction

Ever since the discovery of homogeneous bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2)-alkylaluminum catalyst system for ethylene polymerization[1], homogeneous catalysts have assumed importance for a variety of academic as well as applied reasons[2]. Recent discoveries in the area of homogeneous, highly active and stereospecific metallocene-aluminoxane catalysts[3] have stimulated renewed commercial and academic interest in homogeneous catalysts. This is evidenced by the accumulation of the large volume of patented and published literature during the last 15 years.

Features of homogeneous catalysts based on metallocene-MAO are high activities, control over molecular weight distribution, and ability to polymerize a variety of monomers stereospecifically or astereospecifically. Disadvantages of these catalysts are rapid deactivation and high cocatalyst requirements. Various aspects of these catalyst systems such as a) effect of different transition metals b) effect of ligands around transition metal c) effect of reaction conditions and d) effect of hydrogen on ethylene polymerization have been extensively studied in the literature and are discussed in detail in chapter I.

Nevertheless, many aspects of these polymerization such as effect of added trimethylaluminum (TMA) to MAO, catalyst and cocatalyst concentrations, and cocatalyst/catalyst ratios at low concentration of catalyst have not been studied in the prior literature. Additionally comparative data using MAO, tetraisobutyldialuminoxane (TIBDAO) and TMA are not available.

Sterically hindered aryloxy derivatives of aluminum alkyls have been shown to polymerize propylene and isoprene using β-$TiCl_3$ catalyst[4]. However these compounds have not been studied as cocatalysts for ethylene polymerization using metallocene as catalysts.

In this chapter the following aspects of ethylene polymerization using Cp_2ZrCl_2 as catalyst are discussed.

1. Effect of reaction parameters [Al], [Zr], [Al/Zr] and temperature on Cp_2ZrCl_2-MAO catalyzed ethylene polymerization

2. Role of TMA on Cp_2ZrCl_2-MAO-catalyzed polymerization of ethylene
3. Cp_2ZrCl_2-TIBDAO-catalyzed polymerization of ethylene
4. Role of sterically hindered aryloxy derivative of TMA on Cp_2ZrCl_2-TMA catalyzed polymerization of ethylene

4.2 Experimental Section

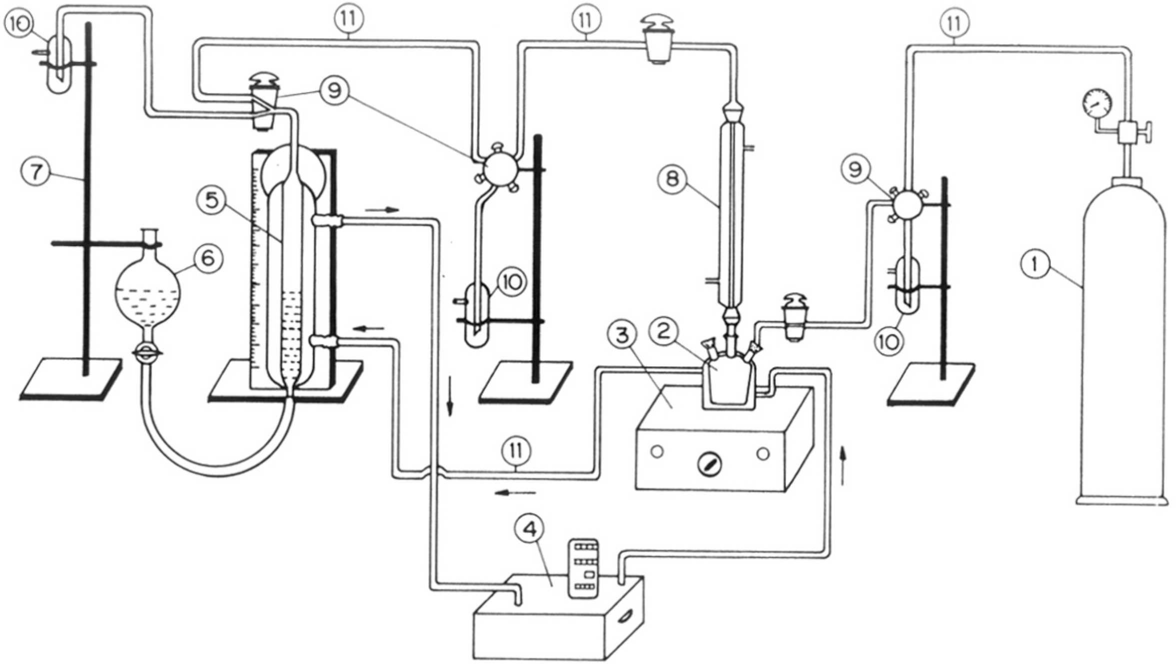
All manipulations involving air sensitive compounds were performed either inside a Labconco model 50004 inert atmosphere glove box continuously purged with high purity N_2 (< 5 ppm moisture) generated using N_2 generator (Spantech, Model, NG 300-1, England) or under a positive pressure of high purity N_2 (<5 ppm moisture; < 5 ppm oxygen) or using standard bench top inert atmosphere techniques[5].

4.2.1 Materials

TMA, MAO (5.5 wt% Al in toluene, [Me]/[Al] = 1.22, TMA content = 11 mol%, average molecular weight = 850) and TIBDAO (3.6 wt% Al) (Schering-A.G., Germany) were used as received. $AlMe(BHT)_2$ cocatalyst, synthesized as described in section 3.2.4 of chapter III, was used for polymerization studies. Polymer grade ethylene was obtained from the Maharashtra Gas Cracker Complex of Indian Petrochemical Corporation Limited at Nagothane, India. It had a moisture content of < 4 ppm (Shaw Model SHA-TR moisture analyzer) and oxygen content of <3 ppm (Braun oxygen analyzer). Toluene (Loba-AR, Bombay) was purified as described in chapter III. Freshly distilled methanol (S.D. Fine Chemical, Bombay) was used.

4.2.2 Description of apparatus used for ethylene polymerization studies under atmospheric pressure (Figure 4.1)

A glass tube (inner diameter = 1.648 cm & length = 117 cm) with a glass jacket, a three way stop cock and a supporting parallel glass tube of length 120 cm was fabricated. The fabricated unit was mounted on a wooden platform of height 150 cm. Graph sheets were pasted on the wooden frame neatly to calibrate the fabricated glass apparatus. Upon calibration, it was found that one unit on graph sheet corresponds to 6.38 mL of ethylene. The calibrated glass tube was used as a gas



1 - ETHYLENE GAS CYLINDER
2 - GLASS REACTOR
3 - MAGNETIC STIRRER
4 - HAAKE WATER BATH
5 - CALIBRATED GAS BURETTE ON WOODEN PLATFORM
6 - SEPARATING FUNNEL WITH SILICON OIL
7 - IRON STAND
8 - GLASS CONDENSER
9 - THREE WAY STOP COCKS
10 - SILICON OIL BUBBLER
11 - POLYETHYLENE PRESSURE TUBING

Fig. 4.1 Ethylene polymerization setup at one atmosphere pressure burette for measuring the difference in displacement of volume of ethylene during the polymerization. A three neck flat bottomed jacketed glass vessel of capacity 70-100 mL was used as the polymerization cell.

A separating funnel of capacity 1000 mL filled with silicone oil (800 mL) was connected through a PVC tubing to the gas burette. The reaction cell was mounted on a magnetic stirrer, which was connected to the gas burette via a T-shaped stopcock using a pressure tubing. Two paraffin bubblers were also connected for evacuation purpose to the reaction assembly and gas burette as shown in the diagram. The reaction cells were dried at 135°C for 12 hours and thoroughly checked for leaks by running a blank experiment under one atmosphere pressure for 2-3 hours. The silicone oil was presaturated with ethylene gas before the start of experiment.

4.2.3 Polymerization of ethylene

Polymerization was performed with the assembly described in section 4.2.2 at one atmosphere pressure of ethylene in toluene. A gas burette with a reservoir containing silicone oil saturated with ethylene was used to feed ethylene continuously to the cell. Toluene was introduced into the cell using a hypodermic syringe. The toluene in the cell was saturated with ethylene. The required amount of cocatalyst (MAO in case of Cp_2ZrCl_2-MAO, TMA in case of Cp_2ZrCl_2-TMA, TMA first and then MAO in case of Cp_2ZrCl_2-MAO + TMA and $AlMe(BHT)_2$ first and then TMA in case of Cp_2ZrCl_2-$AlMe(BHT)_2$+TMA) was introduced using a hypodermic syringe. The temperature was maintained constant both in the reaction cell and in the gas burette by circulating water from a thermostat through the jacket. Polymerization was initiated by addition of Cp_2ZrCl_2 solution after thermostating the whole polymerization system for about half an hour. Consumed ethylene was measured as a function of time. The reaction was terminated by addition of acidified methanol. The polymer was washed several times with methanol, filtered and dried under vacuum to a constant weight. The gas volume measured was corrected for STP to calculate percentage of conversions.

4.2.4 Analysis

Methyl content and aluminum content in MAO and $AlMe(BHT)_2$ were determined using the procedure described in section 3.2.3.1 of Chapter III. Intrinsic viscosities of the polymers were measured at 135°C using decalin as solvent. TGA and DSC of poly(ethylene) were performed on a Perkin-Elmer TGA-7 and Perkin-Elmer DSC-7 Thermal analysis work station respectively.

4.3 Results and discussion

Polymerization of ethylene was studied using Cp_2ZrCl_2 catalyst in combination with various organoaluminum compounds like, TMA, MAO, sterically hindered aryloxy derivative of TMA viz., $AlMe(BHT)_2$ and tetraisobutyldialuminoxane by varying reaction parameters like catalyst concentration, cocatalyst concentration, cocatalyst/catalyst ratio, temperature and by mixing two cocatalysts. The discussion part is divided into four sub sections for the sake of convenience.

4.3.1. Effect of reaction parameters [Al], [Zr], [Al/Zr] and temperature on Cp_2ZrCl_2-MAO catalyzed ethylene polymerization

4.3.2. Role of TMA on Cp_2ZrCl_2-MAO-catalyzed polymerization of ethylene

4.3.3. Cp_2ZrCl_2-TIBDAO-catalyzed polymerization of ethylene

4.3.4. Role of sterically hindered aryloxy derivative of TMA on Cp_2ZrCl_2-TMA catalyzed polymerization of ethylene

4.3.1 Effect of reaction parameters [Al], [Zr], [Al/Zr] and temperature on Cp_2ZrCl_2-MAO catalyzed ethylene polymerization

The reported literature on various reaction conditions on metallocene-MAO catalyzed polymerization of ethylene was discussed in detail in section 1.4, chapter I.

Polymerization of ethylene was performed with Cp_2ZrCl_2-MAO catalyst at different Al/Zr ratios ([Al] was kept constant while changing [Zr] and [Zr] was kept constant while changing [Al] to get various [Al]/[Zr] ratios) and at different temperatures with toluene as reaction medium at a total ethylene pressure of one atmosphere.

In a typical experiment, appropriate amount of cocatalyst, followed by catalyst was injected into a constant known volume of ethylene saturated toluene. The polymerization reaction was followed as a function of time for 30 min.

The catalyst activity, initial rate of polymerization Rp, and intrinsic viscosities of poly(ethylene) at different Al/Zr ratios and temperatures are shown in Tables 4.1 and 4.2.

The conversion of ethylene was in the range of 95-99% for all the polymerization reactions. The catalyst activity and Rp were found to increase with increase in Al/Zr ratios and decrease with Cp_2ZrCl_2 concentration (Table 4.1). It has been reported that the number of active sites [C^*], lies between 75 and 100% of the Zr compounds[6]. Therefore activity should be independent of [Zr][6]. But in reality activity is found to increase with the decrease of catalyst concentration. This is due to the increase of k_p (rate constant of propagation). The catalyst activity is found to be proportional to $[Cp_2ZrCl_2]^{-0.77}$ when log plot of activity versus $[Cp_2ZrCl_2]$ is plotted[6]. This indicates faster propagation at low $[Cp_2ZrCl_2]$.

Chien and Wang[6] as well as Kaminsky[7] *et al.* have reported that zirconocene/MAO catalysts must exist in at least two active forms. These active species will differ by the number of MAO molecules complexed to them[6]. Depending upon the number of MAO molecules complexed to active species k_p, rate constant for propagation, will vary. Chien and Wang have experimentally shown that high activity for low [Zr] and large [MAO] indicate higher k_p for species having larger content of complexed MAO i.e., larger Al/Zr ratios.

Intrinsic viscosities were also found to increase with decrease in Cp_2ZrCl_2 concentration (Table 4.1). Further, catalyst activity and rate of polymerization were found to increase with increase in temperature upto 70°C and then decrease with further increase in temperature to 80°C (Table 4.2). The Cp_2ZrCl_2/MAO catalyst was reported to have maximum activity between 30 and 80°C[6,8] and it decreases at both higher and lower temperatures. This is attributed to increase of both propagation and deactivation with increasing temperature. Chien and Wang have reported the possible mechanism for deactivation[6]. One possibility is a slow dissociation of complexed MAO. (Equation 4.1)

Table 4.1 Ethylene Polymerization Using Cp_2ZrCl_2-MAO Catalyst System[a]: Effect of [Al], [Zr] and [Al]/[Zr]

Entry No.	$[Al].10^2$ (mol/L)	$[Zr].10^7$ (mol/L)	[Al]/[Zr]	Yield (mg)	Catalyst activity (Kg-PE/g-Zr.h.atm)	$Rp.10^{-4}$ (M/Sec)	$[\eta]^b$ (dL/g)
1.	9.51	2.76	344000	280	763	2.98	2.42
2.	9.51	5.53	172000	500	667	2.42	2.36
3.	9.51	8.70	109000	625	531	2.51	2.21
4.	9.51	11.05	86000	620	423	2.03	2.30
5.	2.38	5.53	43000	270	372	1.73	2.41
6.	4.75	5.53	86000	360	482	2.06	2.30
7.	14.26	5.53	258000	500	700	2.56	2.10
8.	4.75	2.90	164000	285	728	2.96	2.51
9.	11.88	7.25	164000	535	546	3.01	1.95
10.	14.26	8.69	164000	670	560	1.85	2.10

[a] temperature = 70°C, toluene = 30 mL, $P_{ethylene}$ = 1 atm; [b] determined in decalin at 135°C

Table 4.2 Polymerization of Ethylene Using Cp_2ZrCl_2-MAO : Effect of Temperature[a]

Entry No.	$[Al].10^2$ (mol/L)	$[Zr].10^7$ (mol/L)	[Al]/[Zr]	Temp. (°C)	Yield (mg)	Catalyst activity (Kg-PE/g-Zr.h.atm)	$Rp.10^{-4}$ (M/Sec)	$[\eta]^b$ (dL/g)
1.	9.51	5.53	172000	50	200	273	0.84	2.90
2.	9.51	5.53	172000	60	380	512	1.71	2.70
3.	9.51	5.53	172000	70	500	667	2.42	2.36
4.	9.51	5.53	172000	80	370	541	1.84	2.20

[a] toluene = 30 mL, $P_{ethylene}$ = 1 atm; [b] determined in decalin at 135°C

C_i^{*}-P ----> C_{i-n}^{*}-P + n MAO (4.1)

Where, C_i^{*} = Active center complexed with "i" number of MAO

The C_i^{*} - 1 is less protected by MAO than C_i^{*} and in fact if i-n = 0, rapid bimolecular deactivation occurs. A second possible deactivation mechanism reported by Chien and Wang[8] is by β-hydride elimination to give metallocene hydride which has a very low propensity for monomer insertion.

At optimum temperature the Ziegler-Natta catalysts have greater propagation rate and less of deactivation, due to which high activity is observed. Above the optimum temperature, rates of propagation as well as deactivation increase and below the optimum temperature rates of propagation as well as deactivation decrease and as a net result low activities will be observed. Intrinsic viscosities were found to be high at lower temperature. This is due to reduced chain transfer at low temperatures.

Rp [moles of ethylene uptake/ (mole of catalyst-Lit. of solvent-sec) = M/sec] versus time plot are shown in Figure 4.2 for different Al/Zr ratios. Within 10 minutes of Cp_2ZrCl_2 addition, maximum Rp was attained which can be seen in Figure 4.2. The Rp steadily increases with time upto 10 - 12 minutes and then decreases to give a decay type kinetic curve. This is due to the bimolecular deactivation of catalyst.

Over the years the following evidences have been reported in the literature in favor of the cationic active species in the homogeneous Ziegler-Natta catalyzed polymerization of olefins.

a) By means of electrodialysis and with the help of an observation of an increase in catalytic activity in polar solvents for Cp_2TiCl_2-$AlMe_2Cl$ catalyst system, Dyachkovskii *et al.* proposed $Cp_2Ti^{+}CH_3$ as the active species[9].

b) With the help of chemical trapping of active species formed for the Cp_2TiCl_2-$AlMeCl_2$ catalyst system with trimethyl(phenylethynyl)silane Eish *et al.* identified $Cp_2Ti^{+}CH_3$ as the active species with $AlCl_4^{-}$ acting as counterion[10].

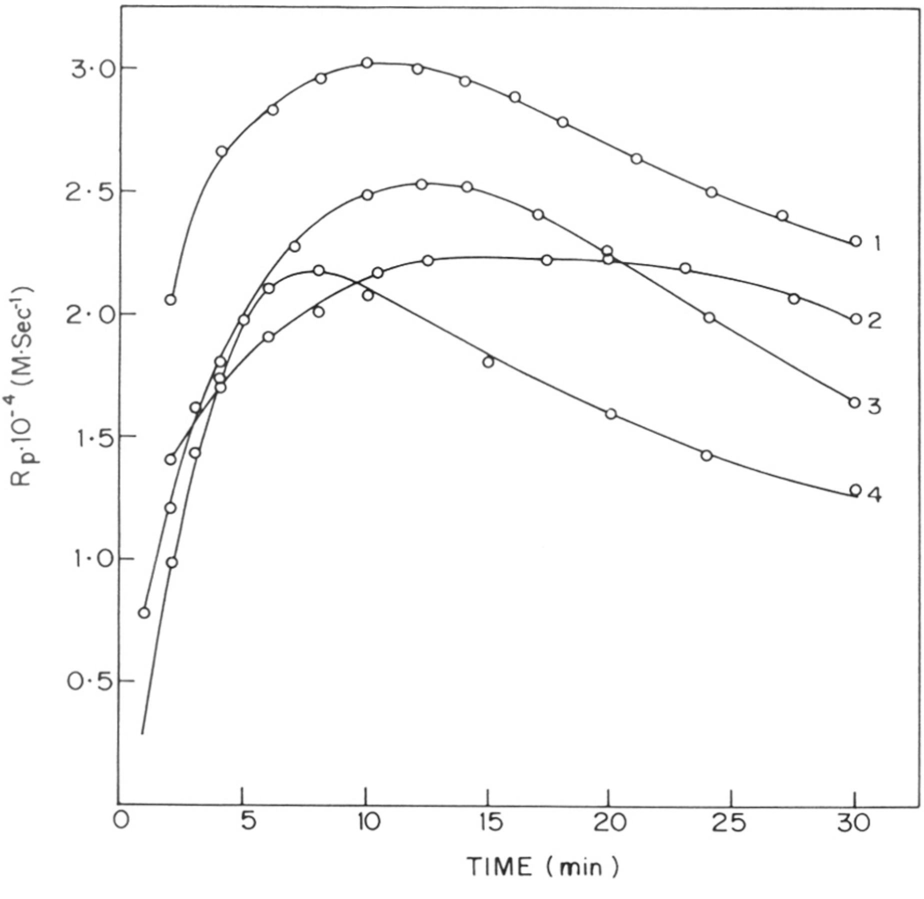


Fig. 4.2 Polymerization of ethylene using Cp_2ZrCl_2-MAO catalyst - Kinetic profile: (1) [Al]/[Zr] = 344000, [Zr] = 2.76×10^{-7} mol/Lit (2) [Al]/[Zr] = 172000, [Zr] = 5.53×10^{-7} mol/Lit (3) [Al]/[Zr] = 109000, [Zr] = 8.70×10^{-7} mol/Lit (4) [Al]/[Zr] = 86000, [Zr] = 11.05×10^{-7} mol/Lit

c) A study of X-ray photoelectron spectroscopy (XPS) (by calculating binding energy values) suggested the $Cp_2Zr^+CH_3$ as the active species with $^-$O-MAO as counterion[11].

d) Based on theoretical calculations (based on PRDDO and ab initio electronic structure calculations) $Cp_2Ti^+CH_3$ cation has been proved as the active species[12].

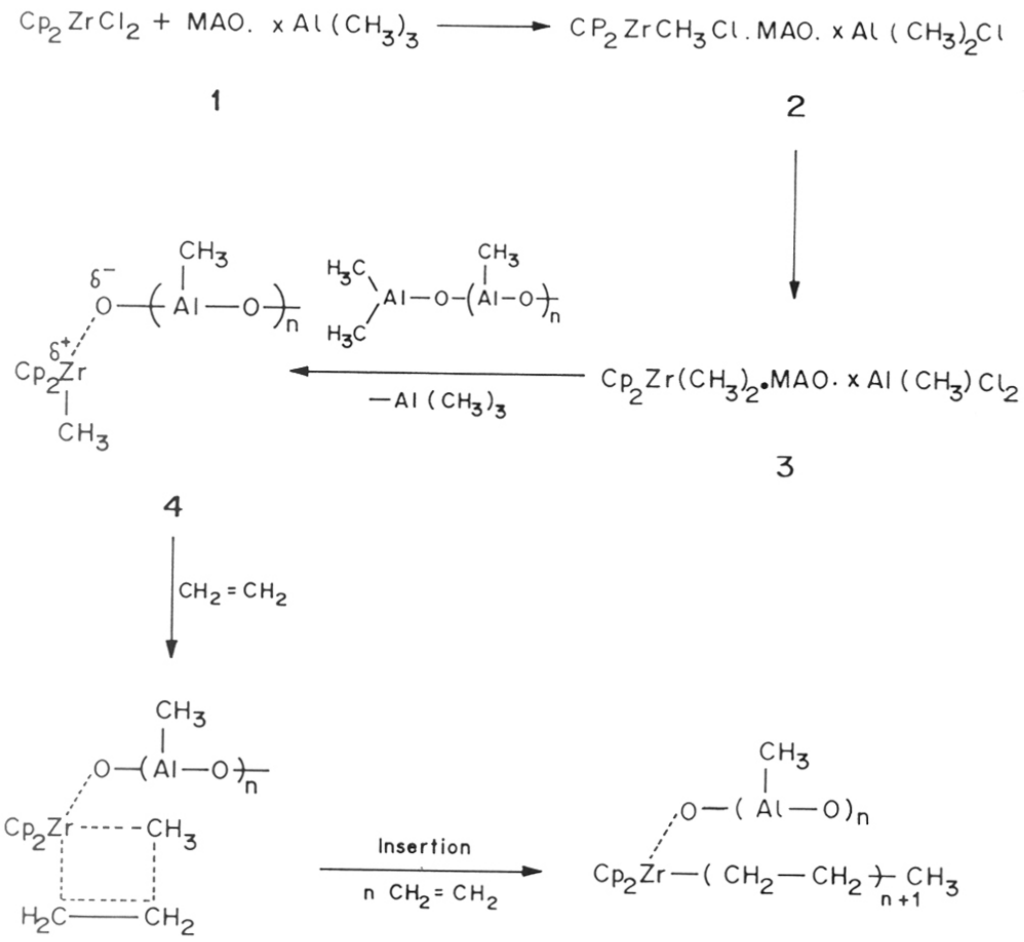
e) ^{13}C CPMAS-NMR spectroscopic studies provided conclusive evidence for existence of a "cation-like" initiating species, $Cp_2Zr^+CH_3$, in the reaction of a metallocene dialkyl and MAO[13,14].

f) The ^1H-NMR studies also provided the evidence for the existence of a "Cation like" active species, $Cp_2Zr^+CH_3$ with $^-O[Al(CH_3)$-O-] counterion for Cp_2ZrCl_2-MAO catalyst system[15,16].

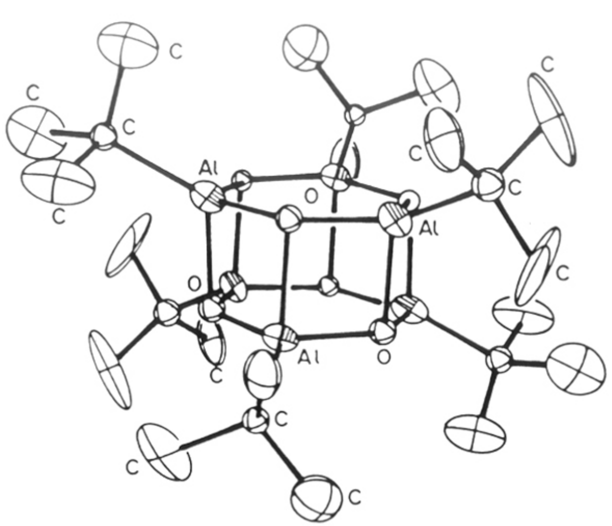
Based on the above evidences, a plausible mechanism for the ethylene polymerization is shown in Scheme 4.1.

The primary reaction step for the formation of the active center is the methylation of the transition metal compound by residual TMA present in MAO. The active species shown in structure 4 of Scheme 4.1 is obviously an over simplification. The influence of MAO is not just limited to alkylation and coordination of the metallocene. Based on the subsequent discussions in this section the active species can be viewed as a cluster of aluminoxane consisting of the cationic metal species inside the cavity of the cluster. Figure 4.3 shows the reported cluster structures of tert-butylaluminoxane. Similar type of cluster structures can also be expected for MAO[17]. Polymerization is initiated by the insertion of ethylene into the metal-C bond, metal bearing a δ^+ charge.

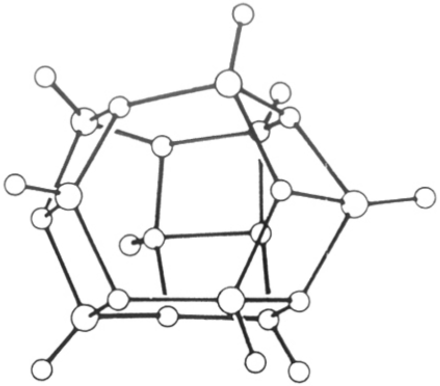
The outstanding cocatalytic effect displayed by the MAO on the metallocene based catalyst system is rather striking and not easy to explain. The presence of Al-O-Al linkages in MAO appears to play a key role in determining the high catalytic activity. This however, is a necessary but not sufficient condition since the system



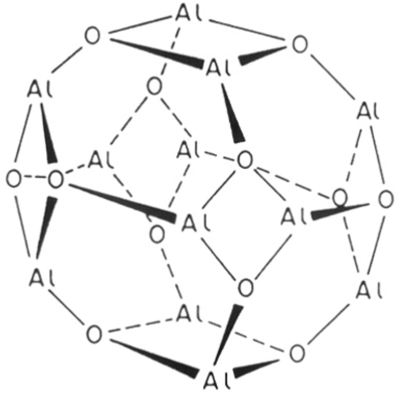
Scheme 4.1 Ethylene polymerization mechanism using Cp_2ZrCl_2-MAO catalyst system



Molecular structure of tert-butylaluminoxane $[(^{t}Bu)Al(\mu_3\text{-}O)]_6$. All the hydrogen atoms are omitted for clarity



Molecular structure of tert-butylaluminoxane $[(^{t}Bu)Al(\mu_3\text{-}O)]_9$. Methyl groups are omitted for clarity



Plausible molecular structure of tert-butylaluminoxane $[(^{t}Bu)Al(\mu_3\text{-}O)]_{12}$. ^{t}Butyl groups are omitted for clarity

Fig. 4.3 Cluster structures of tert-butylaluminoxane

$Cp_2Zr(CH_3)_2/[(C_2H_5)_2Al]_2O$ does not display any catalytic activity in ethylene polymerization[8]. Obviously, one must seek additional explanations for understanding the unique cocatalytic role of MAO.

Based on spectroscopic evidences and X-ray structural studies, Mason[17] *et al.* proposed that MAO and related aluminoxanes $(RAlO)_n$, have cluster structures, similar to those found in the case of iminoalanes, where the aluminum centers are tetra coordinate (Figure 4.3). This is different from the structures of MAO originally proposed, i.e., a linear or cyclic chain structure consisting of alternating aluminum and oxygen atoms, requiring the aluminum to have a co-ordination number of three. This type of a cage structure appears to be uniquely responsible in contributing to the very high cocatalytic activity of MAO. Such cage structures may offer unusual stability to the anion derived by abstraction of a methide group by MAO, by delocalizing the negative charge over a large number of adjacent atoms. Fortuitously, the lewis acidity of the MAO also appears to be finely balanced, not too high, lest it would cause over reduction of the +4 oxidation state of zirconium (the active valence state) nor too low to inhibit the formation of the cationic zirconocene species. The work of Atwood *et al*[18]. on the crystal structure of $[Al_5O_6(CH_3)_{16}]^-$ also points out to the close similarity between the structure of highly oxygenated organoaluminum compound and zeolites. Thus MAO may act as low molecular weight analogs of zeolite type structures. The high productivity of the supported σ-homoleptic complexes R_4M (R = benzyl, trimethylsilyl, neophyl, etc., M = Ti, Zr, Hf) has been ascribed to the presence of Al-O-M bonds[19].

4.3.2 Role of TMA on Cp_2ZrCl_2-MAO catalyzed polymerization of ethylene

There have been only a few attempts in the literature to examine the role of associated TMA on the nature of catalysis. Resconi and co-workers showed that TMA alone could initiate ethylene polymerization along with various zirconocenes[20]. However, activities and molecular weights were much lower. The activities could be substantially enhanced by using sterically hindered zirconocene and triisobutylaluminum[21]. Gianetti and co-workers studied the molecular weight of ethylene polymerization using $(Ind)_2Zr(CH_3)_2$ and $Cp_2Zr(CH_2C_6H_5)_2$ and MAO at

[Al]/[Zr] = 16600 and at 50°C[8]. Catalyst activity was found to decrease with increasing [TMA]/[MAO] ratios. Molecular weights of poly(ethylene) obtained with $Cp_2Zr(CH_2C_6H_5)_2$ strongly decreased with increasing TMA whereas it was invariant when $(Ind)_2Zr(CH_3)_2$ was used. Ethylene polymerization with Cp_2ZrCl_2/MAO was investigated by progressively replacing MAO with TMA at [Al]/[Zr] = 1970[22]. With increasing addition of free TMA to MAO, both catalyst activity and molecular weight decreased. The kinetic profile of the catalyst was not substantially altered upto a [TMA]/[MAO] ≤ 10. At [TMA]/[MAO] = 100, the rate profile changed from a decay to a build up curve.

We have found that addition of TMA to MAO under specified conditions leads to a dramatic increase in catalyst activity as well as catalyst life time. For the sake of comparison polymerization of ethylene was carried out with three different catalyst systems namely, Cp_2ZrCl_2-TMA (I), Cp_2ZrCl_2-MAO (II) and Cp_2ZrCl_2-MAO+TMA (III) in toluene at 70°C. The Cp_2ZrCl_2 concentration ranged from 1.15×10^{-5} to 1.15×10^{-7} mol/L. Three ratios of [Al]/[Zr] were studied which in the case of TMA and MAO were 1000, 10000, 100000. In the case of experiments with MAO + TMA, $[Al]_{total}/[Zr]$ was varied from 1676 to 167600. However, the free TMA added to MAO, by itself, contributed to an [Al]/[Zr] of 1000, 10000 and 100000, which is essentially similar to the ratio used when TMA alone was used as catalyst. The results are shown in Table 4.3 and are plotted in Figures 4.4 and 4.5.

Thermal analysis of the poly(ethylene) prepared by using Cp_2ZrCl_2-MAO catalyst system is shown in Figures 4.6 (TGA) and 4.7 (DSC). Thermogravimetric analysis of poly(ethylene) showed an initial decomposition temperatrue (IDT) of 430°C and final decomposition temperature (FDT) of 478°C. DSC shwoed a Tm of 133.3°C

The Cp_2ZrCl_2-TMA system shows relatively poor catalyst activity and low initial rates of polymerization. Both the rate and catalyst activity increase with increasing [Al]/[Zr] ratio. The Cp_2ZrCl_2-MAO system shows a similar behavior except that the absolute magnitudes of both the rate and catalyst activity are higher. Addition of TMA causes a dramatic increase in catalyst activity (Table 4.3 Entry Nos. 7-9).

Table 4.3 Ethylene Polymerization Using Cp_2ZrCl_2-Organoaluminum Compounds[a]

Entry No.	Al compound	[Me]/[Al]	$[Al]_{total}.10^2$ (mol/L)	$[Zr].10^7$ (mol/L)	$[Al]_{total}/[Zr]$	Time (min)	$Rp.10^{-2}$ (M/Sec)	Catalyst activity (Kg-PE/g-Zr.h.atm)	$[\eta]^b$ (dL/g)
1.	TMA	3.00	1.15	115.00	1000	120	0.55	3.9	1.59
2.	TMA	3.00	1.15	11.50	10000	120	2.50	7.2	1.41
3.	TMA	3.00	1.15	1.15	100000	120	5.65	13.2	1.51
4.	MAO	1.22	1.15	115.00	1000	9	12.87	4.7[c]	1.18
5.	MAO	1.22	1.15	11.50	10000	30	68.24	20.5[d]	2.31
6.	MAO	1.22	1.15	1.15	100000	60	89.81	136.2	2.67
7.	MAO + TMA	2.20	1.15+0.78	115.0	1676	50	20.65	14.5[e]	1.57
8.	MAO + TMA	2.20	1.15+0.78	11.50	16760	120	52.14	77.9	1.69
9.	MAO + TMA	2.20	1.15+0.78	1.15	167600	120	62.87	205.3	2.50

[a] polymerization conditions: temperature, 70°C, toluene = 30 mL, $P_{ethylene}$ = 1 atm. [b] in decalin at 135°C. [c] Reaction ceased after 9 min. [d] Reaction ceased after 30 min. [e] Reaction ceased after 50 min.

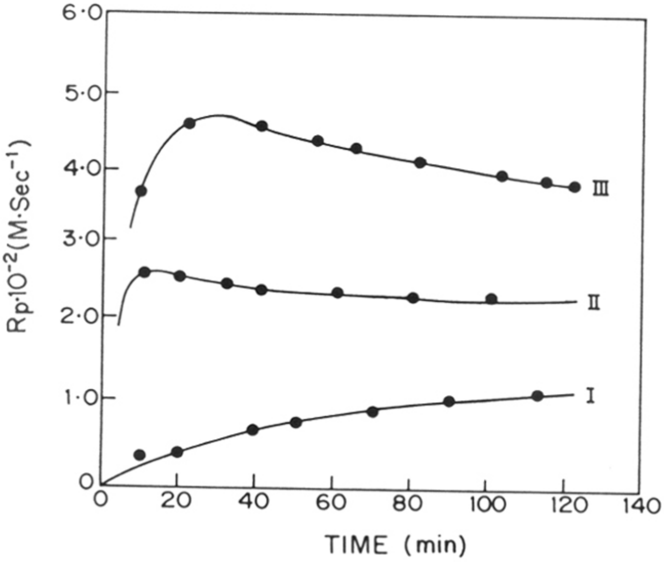


Fig. 4.4 Polymerization of ethylene using Cp_2ZrCl_2-TMA catalyst - Kinetic profile: (I) [Al]/[Zr] = 1000, [Zr] = 1.15×10^{-5} mol/Lit (II) [Al]/[Zr] = 10000, [Zr] = 1.15×10^{-6} mol/Lit (III) Al]/[Zr] = 100000, [Zr] = 1.15×10^{-7} mol/Lit

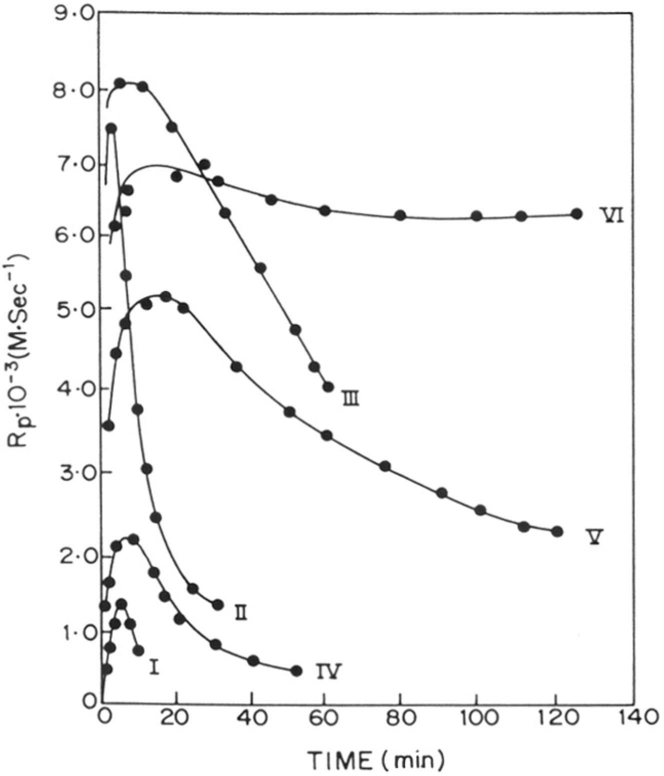


Fig. 4.5 Polymerization of ethylene using Cp_2ZrCl_2-MAO and Cp_2ZrCl_2-MAO+TMA catalysts - Kinetic profile: (I) $[Al]_{MAO}/[Zr]$ = 1000, [Zr] = 1.15 x 10^{-5} mol/Lit (II) $[Al]_{MAO}/[Zr]$ = 1000, [Zr] = 1.15 x 10^{-6} mol/Lit (III) $[Al]_{MAO}/[Zr]$ = 1000, [Zr] = 1.15 x 10^{-7} mol/Lit (IV) $[Al]_{total}/[Zr]$ = 1676, [Zr] = 1.15 x 10^{-5} mol/Lit (V) $[Al]_{total}/[Zr]$ = 16760, [Zr] = 1.15 x 10^{-6} mol/Lit (VI) $[Al]_{total}/[Zr]$ = 167600, [Zr] = 1.15 x 10^{-7} mol/Lit

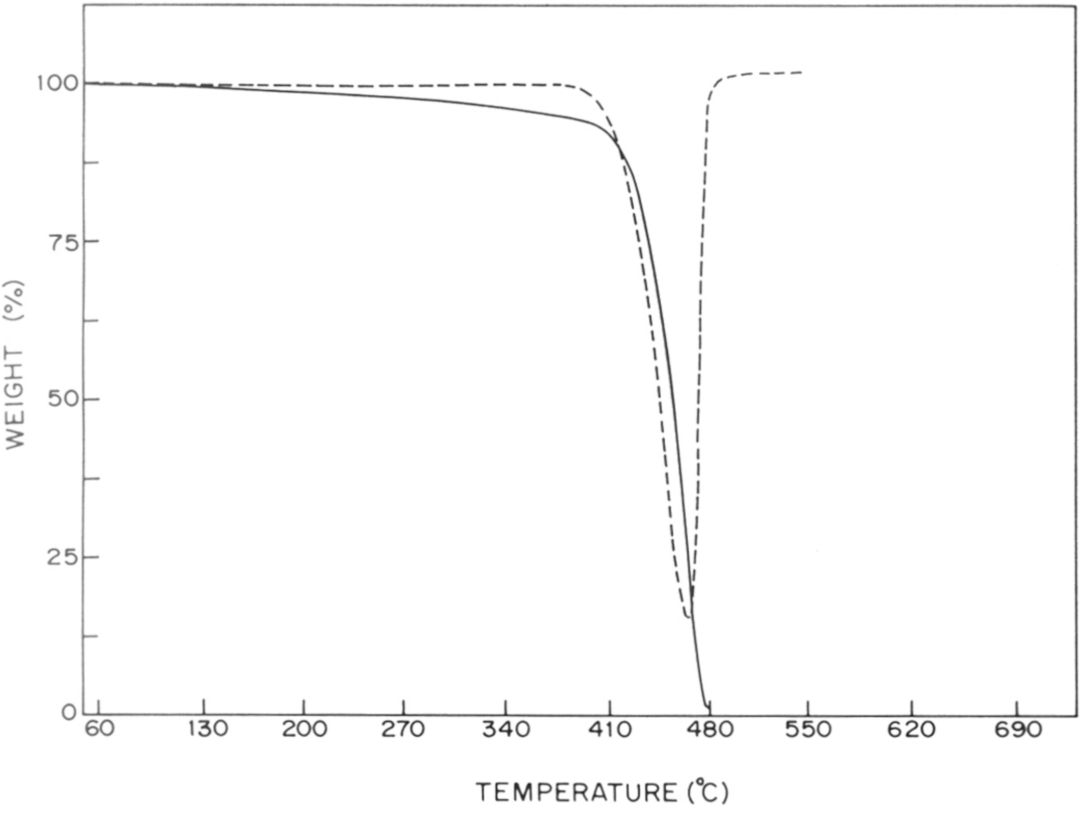


Fig. 4.6 Thermogram of poly(ethylene)

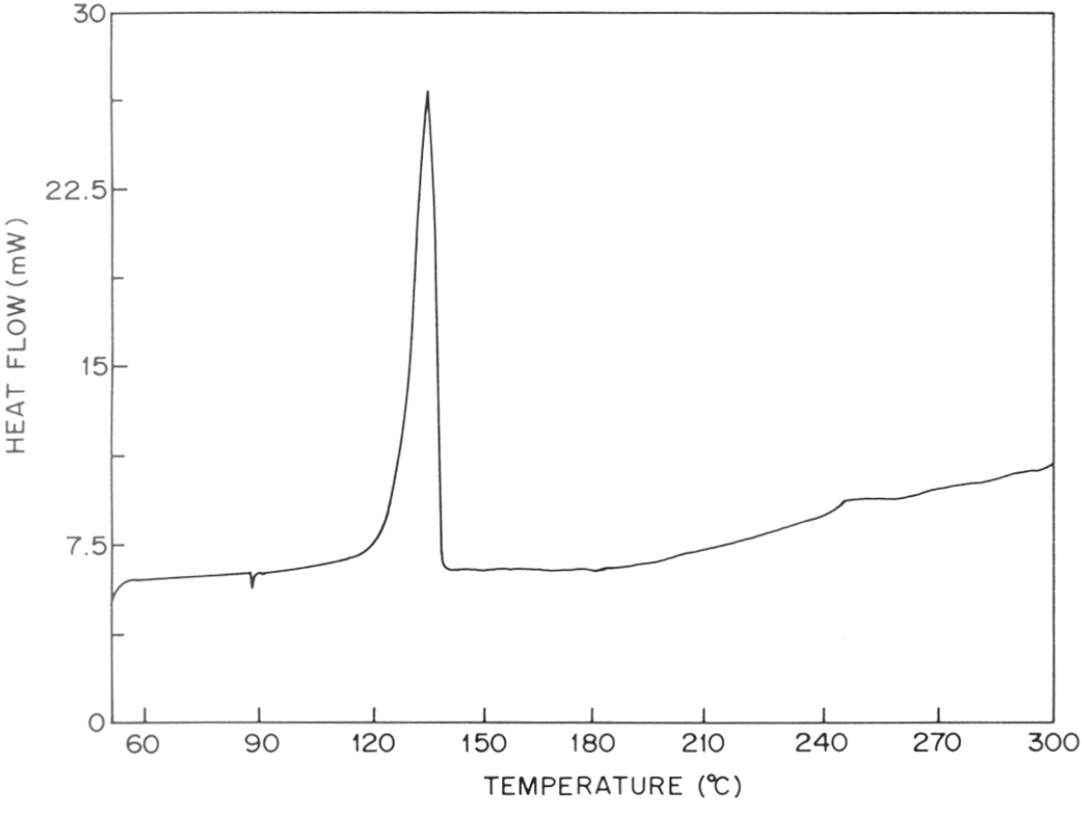


Fig. 4.7 DSC endotherm of poly(ethylene)

The changes in the kinetic profile of the polymerization (Figures 4.4 and 4.5) upon addition of TMA to MAO are more revealing of the subtle yet substantive role played by TMA. TMA alone with Cp_2ZrCl_2 shows a steady-state build up type kinetic curve, especially at [Al]/[Zr] ratio of 1000 and 10000. The onset of a moderate rate decay is evident at [Al]/[Zr] = 100000 (Figure 4.4). MAO alone shows a decay type kinetic curve, the rate of decay being faster at lower [Al]/[Zr] ratios (Figure 4.5). The peak rate is achieved within 5 -10 minutes and thereafter rapid decay of the rate occurs. Decay type kinetic curves for ethylene polymerization using Cp_2ZrCl_2-MAO have been reported earlier in the literature [Figures 4.8[6] and 4.9[23]]. Addition of TMA to MAO slightly reduces the peak rate. However, with addition of TMA, the kinetic profile changes from a decay type to a build up type curve. At a $[Al]_{total}/[Zr]$ ratio of 167000 (Figure 4.5 curve VI) the rate shows negligible decay, exhibiting essentially a steady-state kinetic behavior for over 2h. Such a beneficial effect of added TMA in a MAO/metallocene catalyst system from the point of view of practical catalysis is not explicitly evident in the prior literature. Interestingly and contrary to data published in prior literature, molecular weight is only marginally depressed by addition of free TMA to MAO, under the conditions of this study. The role of TMA has to be seen in the context of the reported mechanism for deactivation of metallocene/MAO complexes. Fisher and Mulhaupt[24] have proposed a two stage deactivation process for Cp_2ZrCl_2-MAO catalyst system, for propylene polymerization.

$$2C^{*} \rightleftharpoons I_1 \longrightarrow I_2 \quad (4.2)$$

The catalytically active complexes C^* are deactivated by a reversible followed by an irreversible process to form inactive species I_1 and I_2. Alkylation and dealkylation are reversible reactions which comprise the equilibrium reaction (Equation 4.2) between C^* and I_1 whereas reduction of the transition metal and formation of lower valent inactive species represent the irreversible conversion of I_1 to I_2.

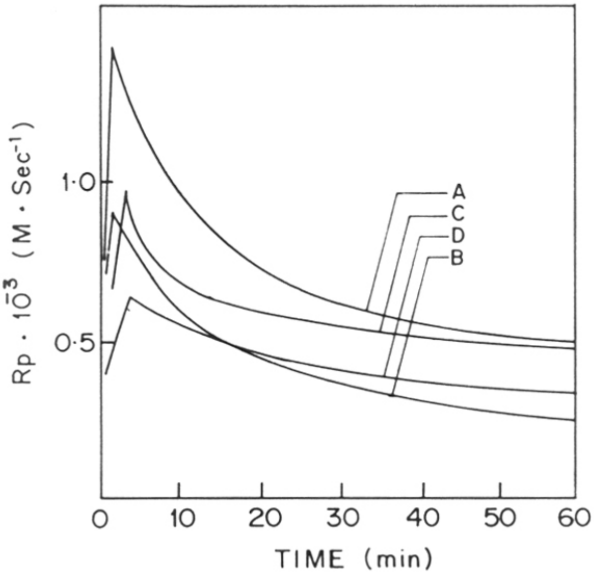


Fig. 4.8 Ethylene polymerization profile for Cp_2ZrCl_2-MAO catalyst: (A) 70°C (B) 50°C for Cp_2HfCl_2 (C) 70°C (D) 50°C, [TM] = 48 μM, [Al] = 56 mM, $P_{(ethylene)}$ = 1.7 atm

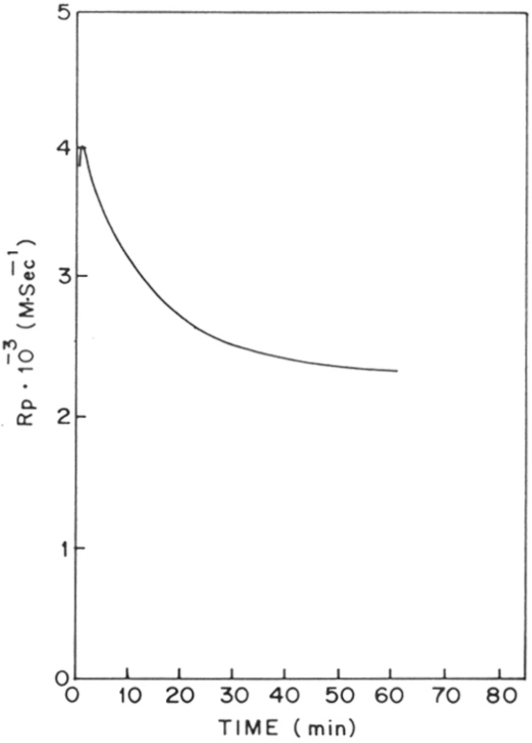
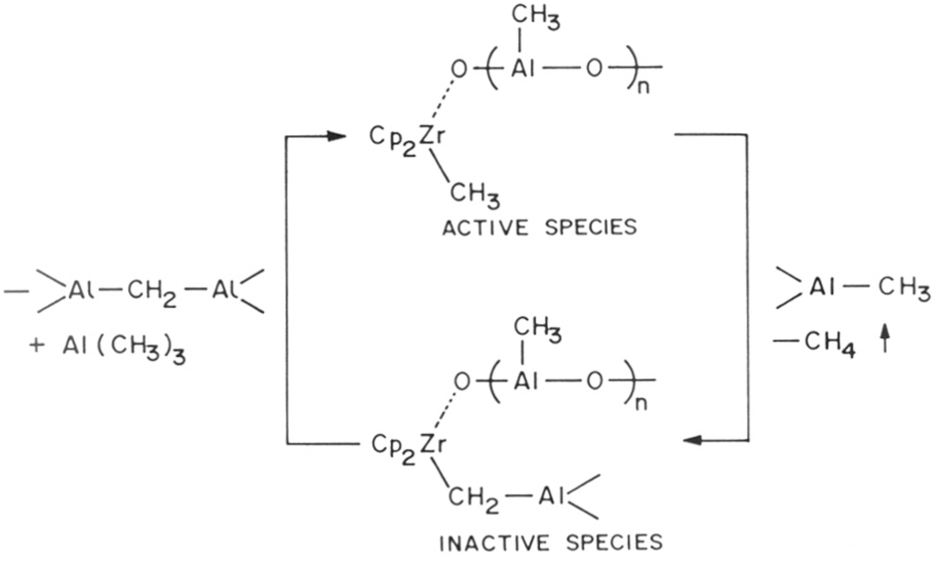


Fig. 4.9 Ethylene polymerization profile for Cp_2ZrCl_2-MAO catalyst

According to Fisher and Mulhaupt the deactivation is initiated by a dealkylation process. Our experiments indicate that the presence of TMA along with MAO keeps the catalyst highly active for over 2 hours (Figure 4.5, curve VI) as compared to a rapid deactivation of the catalyst system in the absence of TMA (Figure 4.5, curve III). It therefore appears that the presence of trialkylaluminum shifts the equilibrium proposed by Fisher and Mulhaupt[24] (Equation 4.2) to the left thus preventing a rapid decay of the active complex.(Equation 4.3)

$$C^* \overset{\text{TMA}}{\rightleftharpoons} I_1 \longrightarrow I_2 \qquad (4\cdot 3)$$

Kaminsky *et al.* have proposed that a competing reaction between zirconocene and MAO leading to methane evolution also causes loss of catalyst activity (Scheme 4.2). Added TMA can also, in principle suppress this reaction. Inactive Zr-CH_2-Al species can be converted to active Zr^+CH_3 species by a transmetallation reaction with TMA with concomitant elimination of Al-CH_2-Al type compound.



Scheme 4.2 Mechanism showing the transmetallation reaction in presence of TMA for the Cp_2ZrCl_2-MAO catalyst system

The possibility that TMA may also be acting to some extent as a scavenger of impurities capable of deactivating the catalyst cannot be ruled out. However, we feel that this is not the only role played by added TMA. Whereas impurities can reduce catalyst activity, it is unlikely to change the nature of the kinetic curve. Such profound changes in kinetic curves must be due to some fundamental processes that either stabilize the active center or prevents it from rapidly decaying.

4.3.3 Cp_2ZrCl_2-Tetraisobutyldialuminoxane (TIBDAO) catalyzed polymerization of ethylene

There are very few reports in the literature regarding the polymerization of ethylene using Cp_2ZrCl_2-TIBDAO. A catalyst activity of 175 Kg-PE/g-Zr-h-atm was reported for ethylene polymerization using $Cp_2Zr(CH_3)_2$-TIBDAO catalyst system at a [Zr] of 3.0×10^{-6} mol/L, Al/Zr of 1700 and at 70°C and at 8 bar ethylene pressure[25].

To understand some of the features of Cp_2ZrCl_2-TIBDAO catalyst system, ethylene polymerization was carried out in toluene at different Al/Zr ratios and temperatures, at one atmosphere pressure of ethylene. In a typical polymerization experiment, appropriate amount of cocatalyst, followed by catalyst was injected into a constant known volume of ethylene saturated in 30 mL of toluene. Polymerizations were carried out at 70°C at Cp_2ZrCl_2 concentration of 11.5×10^{-5}, 1.15×10^{-5} and 0.115×10^{-5} mol/L corresponding to three ratios of [Al]/[Zr] viz., 100, 1000, 10000 at 1.15×10^{-2} mol/L of TIBDAO. Polymerizations were carried out at temperatures 50°C, 60°C and 70°C at [Zr] of 0.115×10^{-5} and [Al]/[Zr] of 10000. The polymerization was followed as a function of time. The results are summarized in Table 4.4 and graphically plotted in Figure 4.10.

The catalyst activity and rate of polymerization Rp were found to increase with increase in Al/Zr or with decrease in Cp_2ZrCl_2 concentration. This is also true in the case of Cp_2ZrCl_2-MAO catalyst system. Activities were found to be in the range of 1 to 6 Kg.PE/g-Zr-h-atm which is very poor as compared to Cp_2ZrCl_2-MAO catalyst system. Similarly, rate of polymerization was also found to be lower when compared to MAO cocatalyzed ethylene polymerization. The lower catalyst activity observed for Cp_2ZrCl_2-TIBDAO system compared to Cp_2ZrCl_2-MAO system is a reflection of the differences in the structure between MAO and TIBDAO. TIBDAO has been

Table 4.4 Ethylene Polymerization Using Cp_2ZrCl_2-TIBDAO Catalyst System[a]

Entry No.	$[Al].10^2$ (mol/L)	$[Zr].10^5$ (mol/L)	[Al]/[Zr]	Temp. (°C)	Catalyst activity (Kg-PE/g-Zr.h.atm)	$Rp.10^{-4}$ (M/sec)	$[\eta]^b$ (dL/g)
1.	1.15	11.5	100	70	0.6	0.93	2.21
2.	1.15	1.115	1000	70	2.7	4.14	2.20
3.	1.15	0.115	10000	70	5.6	7.35	2.45
4.	1.15	0.115	10000	50	2.0	2.81	3.12
5.	1.15	0.115	10000	60	3.5	5.12	2.85

[a]toluene = 30 mL, $P_{ethylene}$ = 1 atm; [b]determined in decalin at 135°C

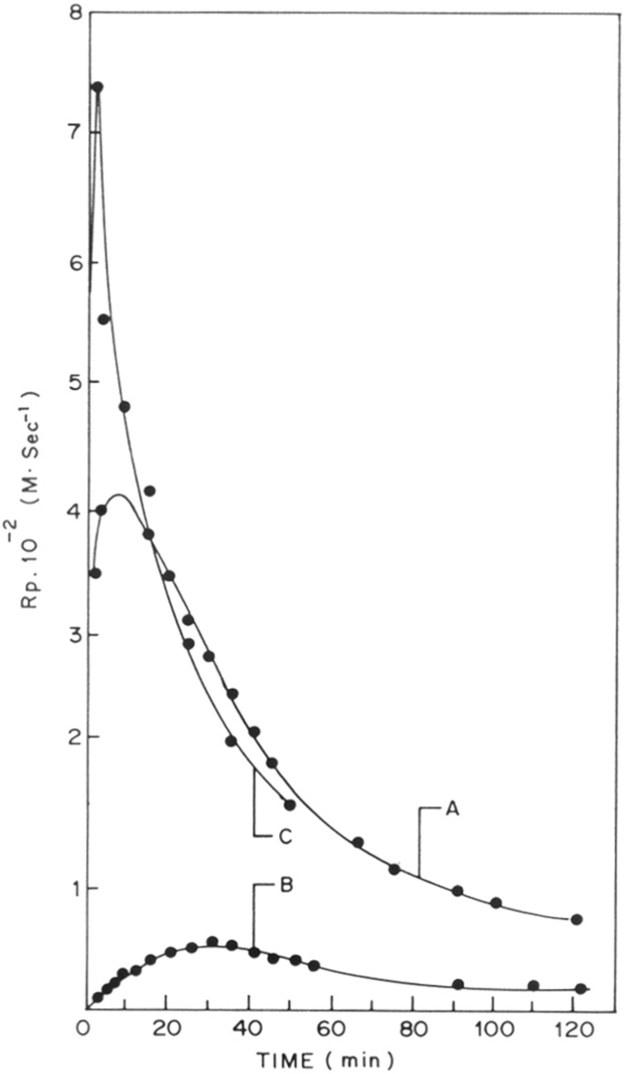
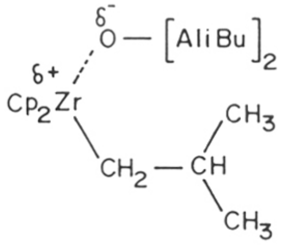


Fig. 4.10 Polymerization profile of ethylene using Cp_2ZrCl_2-TIBDAO catalyst: (A) [Al]/[Zr] = 100, [Al] = 1.15×10^{-2} mol/Lit (B) [Al]/[Zr] = 1000, [Al] = 1.15×10^{-2} mol/Lit (C) [Al]/[Zr] = 10000, [Al] = 1.15×10^{-2} mol/Lit

shown to possess a simple dimeric structure[26] as oligomerization is prevented by the stericallly hindered isobutyl group. Apparently such a structure is not ideal for producing a cocatalyst with optimum activity. Catalyst activity as well as rate of polymerization were found to increase with increase in temperature. Higher molecular weights were observed at lower temperature polymerizations. This is due to the reduced chain transfer at low temperatures. A plot of rate of polymerization versus time is shown in Figure 4.10. The maximum rate was attained within 10 minutes of Cp_2ZrCl_2 addition. A decay type kinetic profile was observed similar to that of Cp_2ZrCl_2-MAO catalyzed ethylene polymerization.

An active species similar to that proposed for the Cp_2ZrCl_2-MAO catalyst system appears possible in the case of Cp_2ZrCl_2-TIBDAO (Structure 4.1). The low catalyst acttivities and low Rp observed for Cp_2ZrCl_2-TIBDAO may be a consequence of the simple structure of TIBDAO compared to a cage or cluster type structure of MAO.



Structure 4.1 Active center of the Cp_2ZrCl_2-TIBDAO catalyst system

4.3.4 Role of sterically hindered aryloxy derivative of TMA on Cp_2ZrCl_2-TMA catalyzed polymerization of ethylene

Sterically hindered aryloxy derivative of TMA, viz., $AlMe(BHT)_2$ failed to initiate the polymerization of ethylene in conjunction with Cp_2ZrCl_2. When TMA was added to the Cp_2ZrCl_2-$AlMe(BHT)_2$ solution, catalytic activity was observed. However, the kinetic profile for ethylene polymerization using Cp_2ZrCl_2-$AlMe(BHT)_2$ + TMA system is different from that of Cp_2ZrCl_2-TMA catalyzed ethylene polymerization.

Ethylene polymerization was conducted at atmospheric pressure at 70°C in a jacketed reaction cell connected to a one Lit gas buret. In the case of Cp_2ZrCl_2-$AlMe(BHT)_2$ + TMA catalyzed ethylene polymerization the desired amount of TMA was added to toluene solution of $AlMe(BHT)_2$ just prior to the addition of Cp_2ZrCl_2. The reaction was initiated by the addition of Cp_2ZrCl_2 solution.

For the sake of comparison polymerization of ethylene was carried out with two different catalyst systems, namely, Cp_2ZrCl_2/TMA (I) and $Cp_2ZrCl_2/AlMe(BHT)_2$ + TMA (II) in toluene at 70°C. Polymerizations were carried out at Cp_2ZrCl_2 concentration of 1.15×10^{-5} and 1.15×10^{-6} mol/L. Four ratios of [Al]/[Zr] viz., 220, 820, 1000 and 2530 at 1.15×10^{-5} mol/L of Cp_2ZrCl_2 concentration and [Al]/[Zr] of 10,000 at 1.15×10^{-6} mol/L of Cp_2ZrCl_2 concentration were studied in the case of I. The same number of polymerizations were carried out in presence of 1.42×10^{-2} mol/L of $AlMe(BHT)_2$ to give $[Al]_{total}/[Zr]$ ratio of 1450, 2050 and 3760 at [Zr] 1.15 x 10^{-5} mol/L as also in presence of 0.78×10^{-2} mol/L of $AlMe(BHT)_2$ to give a $[Al]_{total}/[Zr]$ ratio of 1676 at [Zr] 1.15×10^{-5} mol/L and at $[Al]_{total}/[Zr]$ 16760 at 1.15×10^{-6} mol/L of [Zr].

The results are shown in Table 4.5 and plotted in Figures 4.11 and 4.12.

The Cp_2ZrCl_2/TMA system both in presence and absence of $AlMe(BHT)_2$, shows similar catalyst activity. Both rate and catalyst activity were found to increase with increasing [Al]/[Zr] in presence and absence of $AlMe(BHT)_2$ system. The only difference between the two systems was that in presence of $AlMe(BHT)_2$ the kinetic profile of polymerization (Figures 4.11 and 4.12) showed a discernable change. Cp_2ZrCl_2/TMA shows a steady-state build up type kinetic curve (Curves I and II of Figure 4.11 and curves I, II, III of Figure 4.12). Upon addition of $AlMe(BHT)_2$ the initial rate, Rp increases and the kinetic profile changes from a build up type to a decay type. This decay type kinetic profile shown in the presence of $AlMe(BHT)_2$ (curves III & IV of Figure 4.11 and curves IV, V and VI of Figure 4.12) is reminiscent of Cp_2ZrCl_2-MAO catalyzed polymerization of ethylene at similar Al/Zr ratios. The rationale for the difference in the kinetic profile between Cp_2ZrCl_2-$AlMe(BHT)_2$ + TMA and Cp_2ZrCl_2-TMA could be ascribed to the superior methide abstraction

Table 4.5 Ethylene Polymerization Using Zirconocene-Organoaluminum compounds[a]

Entry No.	Al compound	[Me]/[Al]	$[Al]_{total}.10^2$ (mol/L)	$[Zr].10^5$ (mol/L)	$[Al]_{total}/[Zr]$	$Rp.10^{-2}$ (M/Sec)	Catalyst activity (Kg-PE/gZr.h.atm)	$[\eta]^b$ dL/g
1.	TMA	3.0	1.15	0.115	10000	2.5	7.21	1.41
2.	TMA	3.0	1.15	1.15	1000	0.55	3.94	1.59
3.	TMA	3.0	0.25	1.15	220	0.073	0.86	-
4.	TMA	3.0	0.95	1.15	820	0.12	1.09	1.41
5.	TMA	3.0	2.9	1.15	2530	0.30	4.23	1.43
6.	$AlMe(BHT)_2$ + TMA	2.2	0.78 + 1.15	0.115	16760	7.5	6.57	1.66
7.	$AlMe(BHT)_2$ + TMA	2.2	0.78 + 1.15	1.15	1676	2.04	3.24	1.48
8.	$AlMe(BHT)_2$ + TMA	1.3	1.42 + 0.25	1.15	1450	0.58	0.79	-
9.	$AlMe(BHT)_2$ + TMA	1.8	1.42 + 0.95	1.15	2050	0.78	1.08	1.34
10.	$AlMe(BHT)_2$ + TMA	2.4	1.42 + 2.9	1.15	3760	1.81	4.30	1.40

[a] Toluene = 30 mL, P_{C2H4} = 1 atm, Temperature = 70°C, Time = 120 minutes, [b] in decalin at 135°C

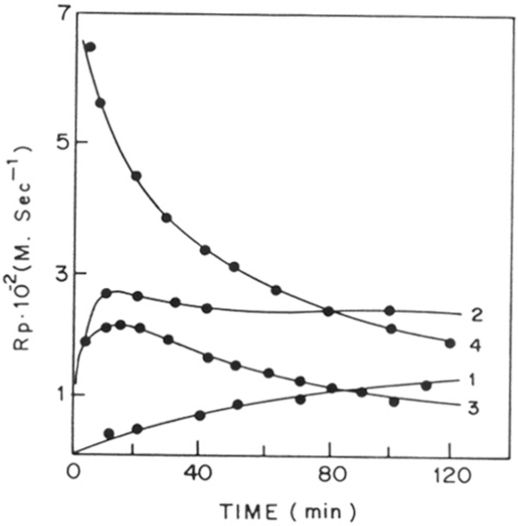


Fig. 4.11 Polymerization profile of ethylene using Cp_2ZrCl_2-TMA and Cp_2ZrCl_2-$AlMe(BHT)_2$+TMA catalyst: (1) $[Al]_{TMA}/[Zr] = 1000$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (2) $[Al]_{TMA}/[Zr] = 10000$, $[Zr] = 1.15 \times 10^{-6}$ mol/Lit (3) $[Al]_{total}/[Zr] = 1676$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (4) $[Al]_{total}/[Zr] = 16760$, $[Zr] = 1.15 \times 10^{-6}$ mol/Lit

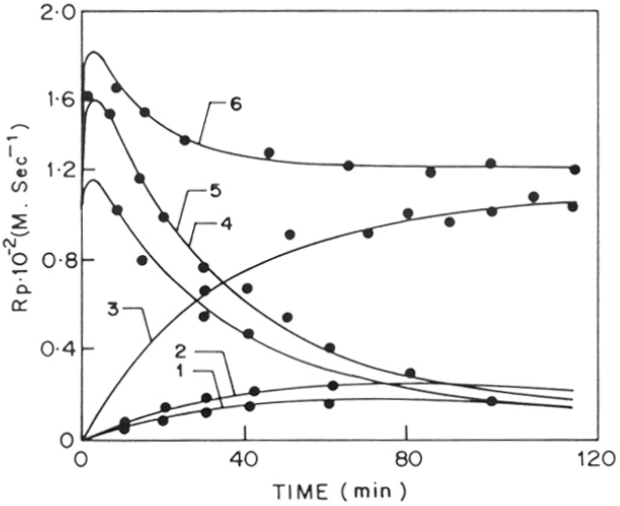


Fig. 4.12 Polymerization profile of ethylene using Cp_2ZrCl_2-TMA and Cp_2ZrCl_2-AlMe(BHT)$_2$+TMA catalyst: (1) $[Al]_{TMA}/[Zr] = 220$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (2) $[Al]_{TMA}/[Zr] = 820$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (3) $[Al]_{TMA}/[Zr] = 2530$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (4) $[Al]_{total}/[Zr] = 1450$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (5) $[Al]_{total}/[Zr] = 2050$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit (6) $[Al]_{total}/[Zr] = 3760$, $[Zr] = 1.15 \times 10^{-5}$ mol/Lit

capacity of $AlMe(BHT)_2$ in which aluminum has a coordination number of 3 and hence a good Lewis acid. The kinetic profile is of a decay type indicating that catalyst deactivation process similar to MAO are also operating in the system.

4.4 Conclusions

These results have significant implications on the metallocene-MAO, catalyzed polymerization of olefins. They establish that the [Me]/[Al] ratio in MAO needs to be suitably adjusted to produce a catalyst of high activity and long life time. This result also has a bearing on the choice of conditions for synthesis of MAO with a defined [Me]/[Al] ratio[8]. Apart from contributing to catalyst activity, TMA plays the more important role of stabilizing the active centers and extending catalyst life time.

$AlMe(BHT)_2$, which is a sterically hindered aryloxide of TMA, is monomeric in nature with a structure similar to oligomeric aluminoxane. It also exhibits a kinetic behavior comparable to that of MAO, although the catalyst activity is far inferior.

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PART B

CHAPTER 5

PHOTOPOLYMERIZATION OF ACRYLIC MONOMERS: A BRIEF INTRODUCTION

5.1 Introduction

Photopolymerization, which involves the utilization of electromagnetic radiation (or light) as the energy source for polymerization of functional monomers, oligomers, and polymers, is the basis of important commercial processes with broad applicability, including photoimaging[1-3], UV curing coatings[4-7] and inks[5-8]. These processes require that light be absorbed by the system and utilized to effect the formation of new chemical bonds. Photopolymerization may be achieved by the utilization of photoinitiators, photocross-linking agents and photocross-linkable polymers.

Photocross-linking agents and photocross-linkable polymers are used primarily in photoimaging applications; photoinitiators are more broadly used in both photoimaging and curing processes.

Photoinitiators absorb light in the UV-visible spectral range (250-450nm) and convert this light energy into chemical energy in the form of reactive intermediates, such as free radicals and reactive cations, which subsequently initiate polymerization of functional monomers and oligomers. The monofunctional monomers form linear polymers, whereas the multifunctional monomers give three dimensional cross-linked networks. In photoinitiating and curing applications, cross-linking imparts solvent resistance. Cross-linked polymer networks are more durable, which is important for protective coatings.

Photopolymerization is the initiation by light of a chain polymerization process. In the more general sense, photopolymerization implies the increase of molecular weight caused by light. Photopolymerization is not only useful for the detection and identification of photochemically produced free radicals, since photopolymerization reactions can be started or stopped at will by the simple expedient of turning on or off light, but also a means is provided for studying the nonsteady state kinetics of polymerization[9]. Photopolymerization also allows for the subtle control of molecular weight and molecular weight distribution by varying the intensity of light. Photopolymerization can be confined to local regions since the light can be spatially controlled. Photopolymerization can be carried out at very low temperatures. Hence, chain-transfer processes leading to branched macromolecules will be absent. Photopolymerization at low temperature yields the low-energy stereospecific polymeric species, namely the syndiotactic configuration of the polymer[10]. Certain monomers can only be polymerized at low temperature, i.e., they have low ceiling temperatures; In such cases photopolymerization is uniquely suitable[11]. Because photopolymerization need not be carried out at elevated temperatures, it has application to biochemistry. One important application of the method is in disk electrophoresis[12]. Photopolymerization played an important role in the early development of polymer chemistry. One of the first procedures for polymerizing vinyl monomers was to expose the monomer to sunlight. Blyth and Hoffman[13] reported the polymerization of styrene by this method in 1845. Photopolymerization initiated by free radical initiators is discussed in the following sections.

5.2 Principles of photopolymerization

5.2.1 Light absorption

The fist step in any photochemical reaction is the absorption of light energy, emitted from a given source, by the photoinitiator or photosensitizer. The probability of light absorption by a molecule is governed by the arrangement of atoms in the molecule and their surrounding environments[14-17]. The UV and visible spectra of photoinitiator or photosensitizer compounds involves electronic transition between π (bonding) and π^* (antibonding) molecular orbitals as well as n (non-bonding) to π^* transitions.

5.2.2 Photophysical Process

After absorption of light energy followed by changes in electron distribution, the excited molecules can undergo various types of photophysical or photochemical deactivation pathways (Figure 5.1).

Most organic molecules have. paired electrons in their ground state (So) and upon absorption of light energy a change in electron distribution takes place in which electrons are prompted to upper singlet level (S1, S2) excited states with conservation of their electron spin configurations. Loss of this absorbed energy without molecular rearrangement can result from internal conversion or through fluorescence radiative process.

A second process, especially important to aliphatic or aromatic carbonyl compounds, is the ability of an excited state molecule (S1, S2 energy levels) to undergo a change in electron spin configuration through intersystem crossing to a lower triplet energy level excited state. Emission of light energy from the triplet level results in phosphorescence radiative process. Another factor to consider is the efficiency with which the incident radiation on the absorbing molecule is converted to the triplet excited state. This efficiency can be defined in the following manner;

$$\Phi_p \text{ (Quantum yield of phosphorescence)} = \frac{\text{Number of triplet states populated}}{\text{Number of quanta absorbed by the molecules}}$$

Photoinitiators or photosensitizers having chemical structures that facilitate intersystem crossing process and enhance Φ_p would be expected to exhibit efficient free radical intermediate generating capabilities[18-20].

5.3 Radical photopolymerization

Vinyl polymerization can be initiated by ionic species as well as by free radicals. Among the various polymerization methods for vinyl and related monomers radical polymerization has been known for the longest time and is best understood. This

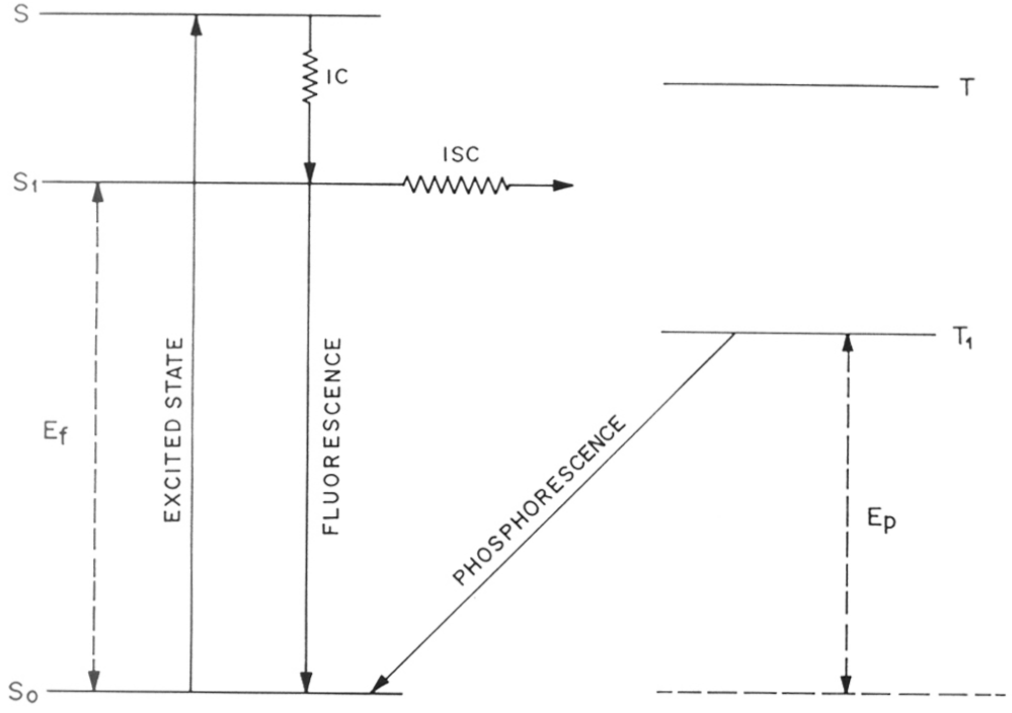


Fig. 5.1 Jablonski diagram

(So = ground state; S = upper singlet level; S1 = lowest singlet level; Ef = energy of lower singlet state; Ep = energy of lowest triplet state; I.C. = radiationless internal conversion process; I.S.C. = radiationless intersystem crossing process) method requires the introduction of a radical species into the monomeric system. The most common way of generating radicals is by homolytic decomposition of covalent bonds. This can be achieved by imparting enough energy to the bond, either by heating or by radiation. Photochemical reactions, either catalyzed or uncatalyzed, can also lead to initiation of free radical polymerization of vinyl and related monomers.

A single free radical can, under favorable circumstances, initiate the polymerization of a thousand molecules. Photochemical production of primary radicals is essentially independent of temperature, unlike thermal free-radical initiators. The free radical is the chain carrier in photopolymerization and the physical properties of the polymer are drastically different from those of the monomer.

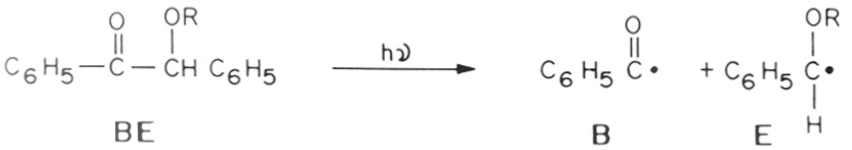
5.3.1 Photoinitiators for radical polymerization

Photoinitiators for radical polymerization generally function by intramolecular bond cleavage, notably cleavage of an aromatic ketone group in the photoinitiator or intermolecular H abstraction from an H donor by the photoinitiator, notably benzophenone, benzil, and quinone derivatives.

5.3.1.1 Intramolecular bond cleavage

An important criterion for photoinitiators of this class is the presence of a bond with a dissociation energy lower than the excitation energy of the reactive excited state. However, the dissociation energy must be sufficiently high to provide thermal stability.

Benzoin ethers represent a useful class of photoinitiators and are utilized in UV curing, predominantly in the area of particle-board finishing. Benzoin ethers (BE) undergo photocleavage to produce benzoyl (B) and benzylether (E) radicals.

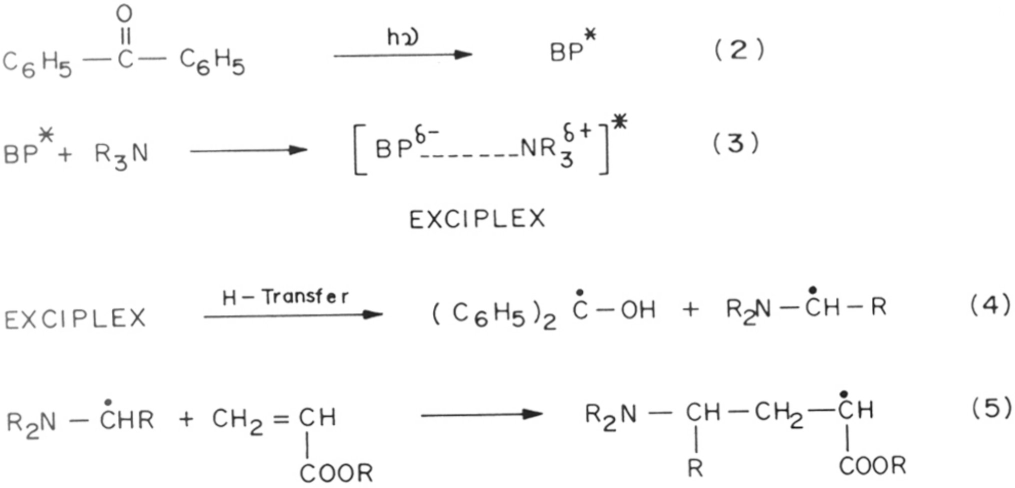


$$\underset{\text{BE}}{C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OR}{\overset{|}{C}H}\;C_6H_5} \xrightarrow{h\nu} \underset{\text{B}}{C_6H_5\overset{O}{\overset{\|}{C}}\cdot} + \underset{\text{E}}{C_6H_5\underset{\underset{H}{|}}{\overset{\overset{OR}{|}}{C}}\cdot} \tag{1}$$

5.3.1.2 Intermolecular H abstraction

In contrast to the above class of initiators, which are capable of generating initiator radicals independently, this type photoinitiators must undergo a bimolecular reaction with H donors. Photoinitiators of this type include benzophenone, thioxanthones, benzil, quinones and Michler's ketone.

Tertiary amines with abstractable α-H atoms are effective H donors for UV curing of acrylate monomers in air. This may be attributed to rapid formation of an excited-state complex (exciplex) between the excited-state photoinitiator and tertiary amines, and initiation of acrylate polymerization by the resulting α-amino radical, as shown below for benzophenone (BP).



$$C_6H_5-\overset{\overset{O}{\|}}{C}-C_6H_5 \xrightarrow{h\nu} BP^* \qquad (2)$$

$$BP^* + R_3N \longrightarrow \left[BP^{\delta-}\text{--------}NR_3^{\delta+}\right]^* \qquad (3)$$

EXCIPLEX

$$\text{EXCIPLEX} \xrightarrow{\text{H-Transfer}} (C_6H_5)_2\,\dot{C}-OH + R_2N-\dot{C}H-R \qquad (4)$$

$$R_2N-\dot{C}HR + CH_2=\underset{COOR}{\underset{|}{CH}} \longrightarrow R_2N-\underset{R}{\underset{|}{CH}}-CH_2-\underset{COOR}{\underset{|}{\dot{C}H}} \qquad (5)$$

Photopolymerization may be considered to consist of four distinct steps. a) The production of radicals b) The initiation of the chain radicals c) The propagation of the chain radical, and d) The removal of the radicals i.e., termination.

5.3.2 The production of radicals

Although thermal decomposition is a common means of generating radicals, it has a disadvantage in that the rate of generation of free radicals cannot be controlled rapidly because of the heat capacity of the system. Photoinitiated polymerization, on the otherhand, can be controlled with high precision, since the generation of radicals can be made to vary instantaneously by controlling the intensity of the initiating light[9]. Light of short enough wavelength (i.e., high enough energy per quantum) can initiate polymerization directly. In general, light absorption results in radical production by either of two pathways.

1. Some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals

   Photoinitiator (PI) ----------> $(PI)^*$ excited state (6)

2. Some compound undergoes excitation and the excited species interacts with a second compound (by either energy transfer or redox reaction) to form radicals derived from the latter and/or former compound(s). The term photosensitizer was originally used to refer to the second pathway, especially when it involved energy transfer, but the distinction has become blurred.

   Photosensitizer (PS) ----> $(PS)^*$ excited state (7)

   $(PS)^*$ + monomer or initiator ------> Free radical formation
   + PS ground state (8)

The mechanism for photoinitiation in a reaction system is not always clear-cut and many involve both pathways. The term photosensitizer is generally referred to any substance that either increases the rate of photoinitiated polymerization or shifts the wavelength at which polymerization occurs.

The rate of photochemical initiation may be expressed as

$Ri = 2\Phi Ia$ (9)

where Ia = intensity of active radiation, Φ is interpreted as quantum yield for chain initiation or radical generation which actually stands for the number of pairs of chain radicals generated per quantum of light absorbed. Photopolymerization may be expressed as

$Rp = (k_p/k_t^{1/2})\ (\varepsilon\ \Phi\ Io)^{1/2}\ [M]^{3/2}$ (10)

ε is the molar absorption coefficient of the active radiation.

The rate of initiation using a photoinitiator I is given by

$Ri = 2\ \varepsilon\ \Phi\ Io(I)$ (11)

and the rate, Rp of the related polymerization is given by

$Rp = k_p/k_t^{1/2}\ (\Phi\ \varepsilon\ Io)^{1/2}\ [I]^{1/2}\ [M]$ (12)

Mechanism for photochemical production of free radical intermediates

For photoinitiators (PI) the primary photochemical reactions are as follows:

$PI + h\nu$ ------> $(PI)_s^*$ Light absorption (13)

$(PI)_s^*$ ------> $PI + h\nu$ Fluorescence (14)

$(PI)_s^*$ ------> $(PI)_T^*$ Intersystem crossing (15)

$(PI)_T^*$ ------> $PI + h\nu$ Phosphorescence (16)

$(PI)_s^*$ or $(PI)_T^*$ -----> $PI_1\bullet + PI_2\bullet$ (Initiating and non-initiating radical intermediates) (17)

where S represents S1, S2.....Sn and T represents T1, T2....Tn

The optimum efficiency of photoinitiation is achieved if all fragment radical intermediates ($PI_1\bullet$ and $PI_2\bullet$) react rapidly with a monomer (M) and start the growth of kinetic chains (Primary initiation)

$PI_1\bullet$ or $PI_2\bullet$ + M $\xrightarrow[\text{(2) Propagation}]{\text{(1) Primary initiation}}$ Polymer (18)

For photosensitizers (PS):

PS + h ν ------> $(PS)_s^{\bullet}$ Light absorption (19)

$(PS)_s^{\bullet}$ -------> $PS^{\bullet}$ + h ν Fluorescence (20)

$(PS)_s^{\bullet}$ -------> $(PS)_T^{\bullet}$ Intersystem crossing (21)

$(PS)_s^{\bullet}$ -------> PS + h ν Phosphorescence (22)

$(PS)_s^{\bullet}$ or $(PS)_T^{\bullet}$ + I (Photo initiator) -------> I• Free radical formation + PS (23)

$(PS)_s^{\bullet}$ or $(PS)_T^{\bullet}$ + SH (Hydrogen donor or substrate) ---------> PSH• + S• (Photo reduction and initiating or non-initiating radical formation) (24)

All free radical intermediates produced through photochemical reactions are primary initiators in that certain structures may be incapable of starting kinetic chain growth of a vinyl monomer.

PI + h ν ----> PI1• + PI2• (25)

$PI_1\bullet$ + M ----> Polymer formation (26)

$PI_2\bullet$ + M ----> No reaction (27)

PS + SH ----> PSH• + S• (28)

S• + M -----> Polymer formation (29)

PSH• + M -----> No reaction (30)

Factors such as solvent and the actual chemical structure of the vinyl monomer (M) may ultimately determine whether or not a primary radical intermediate undergoes initiation or termination processes.

Irradiation of some monomers results in the formation of an excited state M^* by the absorption of light photon (quanta)

$M + h\nu \text{ -----> } M^*$ (31)

The excited species undergoes homolysis to produce radicals

$M^* \text{ ------> } R\bullet + R\bullet'$ (32)

capable of initiating the polymerization of the monomer. The identities of the radicals R• and R•' are not usually well established. Nor it is clear that photolysis of a bulk monomer always results in the simple homolysis to yield two radicals per monomer molecule as described in Equation 32. Initiation by photolysis of a monomer is limited to those monomers where the double bond is conjugated with other groups (e.g., styrene, methyl methacrylate) such that absorption will occur above the vacuum UV region (200 nm) where light sources are readily available.

It is customary, however, to use a photochemical initiator such as benzoin or azoisobutyronitrile, which is decomposed into free radicals by ultravoilet light in the 3600 Å region where direct initiation through decomposition of monomer does not occur. In photopolymerization these initiators are used at temperatures low enough so that they do not undergo appreciable thermal decomposition.

5.3.3 Initiation of the chain radicals

When free radicals are generated in the presence of a vinyl monomer, the radical adds to the double bond with the regeneration of another radical. If the radical formed by decomposition of the initiator I is designated by R•,

$I \text{ -------> } 2R\bullet$ (33)

$(C_6H_5COO)_2 + h\nu \text{ ----> } 2\, C_6H_5COO\bullet \text{ ----> } 2C_6H_5\bullet + 2\, CO_2$ (34)

AIBN + h ν -----> $2(CH_3)_2C^{\cdot}\text{-}CN + N_2$ (35)

R• + $CH_2{=}CHX$ ------> $RCH_2C^{\cdot}(H)(X)$ (36)

The regeneration of the radical is characteristic of chain reactions. The efficiency with which radicals initiate chains can be estimated by comparing the amount of initiator decomposed with the number of polymer chains formed. The most direct method of finding the initiator efficiency depends upon analyzing the polymer for initiator fragments. Most initiators in typical vinyl polymerizations have efficiency between 0.6 and 1.0; that is, between 60 and 100% of all the radicals formed ultimately initiate polymer chains. The major cause of low efficiency is recombination of radical pairs before they move apart[21].

5.3.4 Propagation of the chain radicals

The chain radical formed in the initiation step is capable of adding successive monomers to propagate the chain.

$R\text{-}(CH_2CHX\text{-})_xCH_2\text{-}C^{\cdot}(H)(X) + CH_2{=}CHX$ ---> $R(CH_2CHX\text{-})_{x+1}CH_2C^{\cdot}(H)(X)$ (37)

5.3.5 Termination of the propagating chain radicals

Propagation will continue until the supply of monomer gets exhausted were it not for the strong tendency of radicals to react in pairs to form a paired-electron covalent bond with loss of radical activity. This tendency is compensated for in radical polymerization by the small concentration of radical species compared to monomers.

The termination step can take place in two ways: combination or coupling

$\text{-}CH_2C^{\cdot}(H)(X) + \text{-}CH_2C^{\cdot}(H)(X)$ ------> $\text{-}CH_2C(H)(X)\text{-}C(H)(X)\text{-}CH_2\text{-}$ (38)

or disproportionation;

$\text{-}CH_2C^{\cdot}(H)(X) + \text{-}CH_2C^{\cdot}(H)(X)$ ------> $\text{-}CH_2CH_2(X) + (X)C(H){=}CH\text{-}$ (39)

in which hydrogen transfer results in the formation of two molecules with one saturated and one unsaturated end group. Each type of termination is known. For example, studies[22] of the number of initiator fragments per molecule showed that polystyrene terminates predominantly by combination, where as poly(methyl methacrylate) terminates entirely by disproportionation at polymerization temperatures above 60°C, and partly by each mechanism at lower temperatures.

Radical - Molecule reactions

Although the four steps of radical generation, initiation of a chain radical, propagation of a chain radical and termination of the chain radical are necessary and sufficient for chain polymerization, other steps can take place during polymerization. These often involve the reaction between a radical and a molecule.

Chain transfer

It was recognized by Flory[23] that the reactivity of a radical could be transferred to another species, which would usually be capable of continuing the chain reaction. The reaction involves the transfer of an atom between the radical and the molecule. If the molecule is saturated, like a solvent or other additive, the atom must be transferred to the radical:

$$-CH_2C^{\cdot}(H)(X) + CCl_4 \text{ -----> } -CH_2CH_2\text{-}CH(X)Cl + {\bullet}CCl_3 \qquad (40)$$

If the molecule is unsaturated, like a monomer, the atom transferred (usually hydrogen) can go in either direction;

$$-CH_2C^{\cdot}(H)(X) + CH_2{=}CHX \text{ -------> } \begin{array}{l} -CH_2CH_2X \;+\; CH_2{=}C^{\cdot}(X) \\ \\ -CH{=}CHX \;+\; CH_3C^{\cdot}(H)(X) \end{array} \qquad (41)$$

The major effect of chain transfer to a saturated small molecule (solvent, initiator, or deliberately added chain-transfer agent) is the formation of additional polymer molecule for each radical chain initiated. Transfer to polymer and transfer to monomer with subsequent polymerization of the double bond lead to the formation of branched molecules. The latter reaction has a pronounced effect on molecular weight distribution and is important in the production of graft copolymers. The reactivity of various polymer radicals to transfer varies widely. Transfer reactions offer a valuable means of comparing radical reactivities.

Inhibition and Retardation

Inhibitors are compounds that have very high transfer constants Cs and therefore allow the growth of only a very short polymer chain and produce radicals of such a low reactivity that they cannot restart another polymerization and must decay by recombination. Inhibitors effectively scavenge all reactive radicals in the system and inhibit the polymerization process until they are exhausted. After such an inhibition period, polymerization can proceed in the usual manner. Another class of compounds that has properties similar to those of inhibitors but lower transfer constants Cs allows some polymer formation. Also the reactivity of the transferred radicals may occasionally be sufficient to restart the kinetic chain after some delay. Such compounds do not inhibit polymerization, they only retard it; they are therefore called retardants. There is no clear borderline between inhibitors and retardants; the difference is mainly in the event of their action.

The inhibitors are added to prevent premature polymerization during the storage of monomers; retardants are sometimes added to modify the rate of the reaction. The most popular inhibitors are substituted phenols, hydroquinone, quinone, trinitrobenzene, diphenyl picryl hydrazyl radical or triphenyl methyl radical.

(42)

Most undesirable inhibitor is molecular oxygen. Strictly speaking, molecular oxygen is a retarder, it reacts with radicals to form a peroxy radical.

$P\bullet + O_2 \dashrightarrow P\text{-}O\text{-}O\bullet$ (43)

The peroxy radicals have very low reactivity, but many of them will eventually add to the monomer and reinitiate the chain; the process is retardation.

The added inhibitors are usually also removed from the system before polymerization. The phenolic inhibitors can be extracted by alkaline solutions and the monomer distilled. The monomer is filtered over an active alumina column, and the inhibitor is retained by polar adsorption on this column.

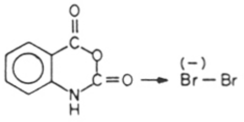
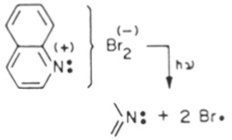
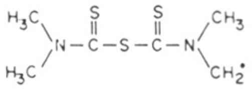
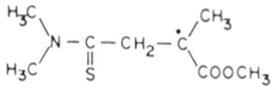
5.4 Photopolymerization of acrylic monomers: Theory

Photoinitiation of free radical polymerization of acrylic monomers by different initiators has received considerable attention in recent years. In the literature, benzoyl peroxide[24], phosphonium[25], sulphonium[26], arsonium[27], nitrogen[28], ylides, metal ylide complexes[29], tetramethylthiuram disulphide[30], quinoline-bromine charge transfer complex[31], isatoicanhydride-bromine donor-acceptor complex[32], isoquinoline-sulphurdioxide charge-transfer complex[33], sulphurdioxide[34], bromine[35], etc., have been used as photoinitiators for the photopolymerization of some acrylic monomers.

Different types of initiators reported for the photopolymerization of acrylic monomers are shown in Table 5.1

Photopolymerization of acrylic monomers are generally performed in the temperature range of 30°C to 60°C using a high pressure mercury lamp emitting light of wavelength in the 360 - 440 nm range. The apparatus used for the photopolymerization is made of borosilicate glass through which the light can pass completely. For kinetic studies the borosilicate made dilatometer was used. Monomer and initiator were mixed in the required proportion, and then irradiated by U.V. light. The monomer-initiator complex formed generates a radical in presence of light which initiates the polymerization.

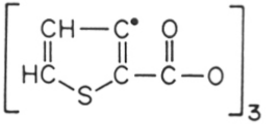
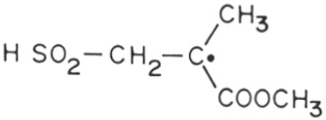
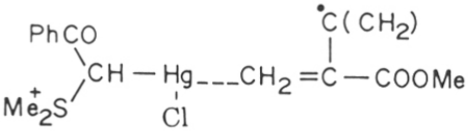
Table 5.1 Photopolymerization of Methyl Methacrylate Using different Initiators

Initiator	Initiating species	Temp. (°C)	Wavelength of irradn. (nm)	k_p^2/k_t (Lit.mol^{-1}. sec)	$[M]^a$	$[I]^a$	E_A (KJ/mol)	Ref.
Isoquinoline SO_2 charge transfer complex	$[\mathrm{IQ}-\mathrm{SO_2}\text{----}\mathrm{MMA}]$	35	440	1.85	1.25	0.51	45	33
Isatoic anhydride Bromine Donor-Acceptor complex		40	-	0.017	0.87 to 1.15	0.32	21	32
Quinoline-Br_2 charge-transfer complex		-	440	0.011	1.0	0.5	14	31
Tetramethyl thiuram disulphide^a		40	420	0.011	1.02 to 1.66	0.5	34	30(a)
Tetramethyl thiuram monosulphide^b		40	420	0.014	1.18 to 1.94	0.5 and 0.16	33	30(b)

^{a}Chaintransfer to initiator = 1; ^{b}chain transfer to monomer = 1.9×10^{-5}

Contd....

Table 5.1 Contd....

Initiator	Initiating species	Temp. (°C)	Wavelength of irradn. (nm)	k_p^2/k_t (Lit.mol^{-1}. sec)	[M][a]	[I][a]	E_A (KJ/mol)	Ref.
Chromium thiophene carboxylate		30	440	0.0004	1.2	0.7	19	29(b)
Bromine	[Br — Br----MMA]	40	440	0.012	-	0.5	16	35
SO_2[a]		40	420	0.014	1.5	0.13	16	34
Phenacyldimethyl sulphonium ylide-mercuric chloide complex		85	Radical	0.033	1.33	0.33	64	29(a)

[a] Chain transfer to monomer = 1.0 x 10^{-5}, chain transfer to initiator = 1.6

Some initiators perform more than one function. Sulphurdioxide shows three distinct roles in the polymerization of vinyl and related monomers a) comonomer for radical polymerization b) catalyst for initiation of polymerization and c) solvent for cationic polymerization. In most of the reported work[36-41] the proportion of sulphurdioxide was high and could not be considered as of catalytic proportion. Matsuda[42] has suggested that, in the polymerization of methyl methacrylate initiation can only be effected when, along with sulphurdioxide (acceptor), a donor compound (such as pyridine, triethylamine) and an organic halide (such as carbontetrachloride) are present. In contrast, Ghosh *et al.* reported some results on bulk and solution polymerizations of methyl methacrylate and a few other vinyl monomers at ambient temperature induced by very low (catalytic) concentrations of sulphurdioxide, used as a lone initiator system and in redox combination with t-butyl hydroperoxide[43-45].

Free radical photopolymerization of vinyl monomers with the use of a halogen alone, i.e., chlorine or bromine, as the photoinitiator under visible or ultravoilet light in aqueous or non aqueous media has been reported in the literature[46]. Sakota[47] *et al.* observed that the photoinduced polymerization of methyl methacrylate and styrene in the presence of bromine proceeds through the formation of 1:1 adduct of bromine and the respective monomers and subsequent photodecomposition of the adduct (monomer dibromide) to free radicals while that of acrylonitrile and ethyl acrylate is brought about directly by bromine. Based on kinetic investigations of photopolymerization of methyl methacrylate in presence of low concentrations of bromine in bulk and diluted (near bulk) systems Ghosh et al., also reported the 1:1 complex formation between methyl methacrylate and bromine which will decompose on irradiation to give a radical initiating species[35].

5.4.1 Kinetics of photopolymerization of acrylic esters

The kinetic parameters like k_p^2/k_t, initiator exponent, monomer exponent for the photopolymerization were determined at a constant temperature and at low conversions (<10%). Mostly dilatometer was used for the kinetic studies which is made from borosilicate glass ampoules and capillaries. The contraction in volume in dilatometer is measured with the help of a cathetometer. The dilatometer is illuminated at required wave length after filling the dilatometer with required amounts of monomer, initiator, and solvent (in case of solution polymerization).

5.4.1.1 k_p^2/k_t value

k_p^2/k_t is an important parameter in the chain polymerization kinetics because the polymerization rate may be predicted for any value of initiation rate from the value of the ratio. It also gives the relative order of polymerization of different monomers at a given rate of chain initiation and its value can be calculated using the following simplified form of Mayo equation.

$$\frac{1}{\bar{P}_n} = 1{\cdot}85 \left(\frac{K_t}{K_p^2}\right) \left(\frac{R_p}{[M]^2}\right) + C_M + C_I \left(\frac{[I]}{[M]}\right) \qquad (44)$$

Where, k_p and k_t are the rate constants for propagation and termination reactions respectively, M stands for monomer and I stands for initiator.

In the most simplified case, i.e., in the absence of any side reactions, a plot of (1/Pn.) vs $(Rp/[M]^2$ would give a straight line, from the slope of which the value of k_p^2/k_t can be obtained. Various k_p^2/k_t values reported for the photopolymerization of acrylic monomers using different photoinitiators are shown in Table 5.1. For methyl methacrylate k_p^2/k_t value is in the range of 0.0108 to 0.033 $L/mol^{-1}sec^{-1}$ for different initiators.

It is obvious that for a given monomer at a given temperature, the average length of the kinetic chain depends primarily on the value of k_p^2/k_t, which depends only on the nature of the polymer[48]. Table 5.2 shows the value of k_p^2/k_t at 60°C for several polymers together with molecular weight estimated for a polymer prepared by bulk polymerization of monomer with the rate of polymerization adjusted (by proper selection of concentration of the initiator) to a convenient value of 1 mol $L^{-1}h^{-1}$. For this calculation, one kinetic chain is assumed to produce one polymer molecule. It is fairly easy to prepare polymers with lower molecular weight by either reducing the concentration of monomer or employing chain transfer agents. However, it is quite difficult to prepare a high molecular weight polymer from a monomer with a low value of k_p^2/k_t.

For methyl methacrylate with k_p^2/k_t value of 0.03 $Lit.mol^{-1}.sec$ the maximum molecular weight one can achieve is 900,000.

5.4.1.2 Initiator exponent

The initiator exponent gives an idea of the kinetics and mechanism of polymerization. Typical value of initiator exponent for radical initiated polymerization of acrylic monomers is 0.5. Photopolymerization of acrylic monomers is carried out at a constant temperature under varying concentration of the photoinitiator and at fixed intensity of the light source to determine the initiator exponent. The slope of the plot of log Rp vs log [initiator] gives the initiator exponent. Initiator exponents reported for various initiators for the photopolymerization of acrylic monomers are shown in Table 5.1.

5.4.1.3 Monomer exponent

The monomer exponent also gives an idea of the kinetics and mechanism of polymerization. Typical monomer exponent value for radical initiated (photo/thermal) polymerization of acrylic monomers is 1.0. The slope of the plot of log Rp vs log [monomer] at a constant temperature and constant initiator

Table 5.2 Values of k_p^2/k_t for Several Polymers at 60°C and Typical Values for their Molecular Weight

Monomer	k_p^2/k_t (Lit.mol^{-1}.sec)	Molecular weight ($\bar{M}n$)
Methyl acrylate	2.0	60,000,000
Vinyl acetate	0.2	6,000,000
Methyl methacrylate	0.03	900,000
Styrene	0.002	60,000

concentration gives the monomer exponent. The monomer exponents reported for various initiators for the photopolymerization of acrylic monomers are shown in Table 5.1.

5.4.1.4 Chain transfer

As discussed earlier, in addition to the usual reaction steps i.e., initiation, propagation and termination, occurrence of certain other side reactions limiting the growth of polymer molecules without really affecting the rate of polymerization is often reported[23]. These reactions are termed as chain transfer reactions. Chain transfer usually lowers the Pn value. A chain transfer reaction proceeds via transfer of the free radical center from a growing chain to a molecule present in the system (initiator, monomer or solvent) to generate a new radical which propagates the chain process in the normal manner. The various chain transfer constants reported for the photopolymerization of acrylic monomers are shown in Table 5.1.

5.4.1.5 Activation energy

Increase of temperature usually increases the polymerization rate and decreases the polymer molecular weight. The quantitative effect of change of temperature is complex, since Rp and Pn depend on a combination of three rate constants, namely k_d, k_p and kt. Each of the rate constants for initiation, propagation and termination can be expressed by an Arrhenius type relationship.

$$K = Ae^{-E/RT} \qquad (45)$$

$$\text{or } \ln k = \ln A - E/RT \qquad (46)$$

Where A is the collision frequency factor, E, the Arrhenius activation energy and T the absolute temperature. One can determine E and A from the slope and intercept of the plot of ln k vs 1/T.

The apparent activation energy E_a for overall polymerization is given by,

$E_a = E_d/2+(E_p-E_t/2)$ (47)

Where the subscripts d, p and t have their usual significance. The activation energy for the spontaneous decomposition of most of the commonly used free radical initiators[24] is in the range of 30-35 kcal mol^{-1}. The E_p and E_t values for most of the monomers are in the range 5-10 kcal mol^{-1} and 2-5 k cal mol^{-1} respectively[24]. The overall activation energy for most of the polymerization initiated by thermal decomposition of initiator is therefore close to 20 k cal mol^{-1}. For purely photochemical initiation, the initiation step is temperature independent, and $E_d = 0$, since the energy for initiator decomposition is supplied by light quanta. The apparent activation energy for overall photopolymerization is about 5 k cal mol^{-1}. This low value of E_a indicates that R_p of photopolymerization will be less sensitive to change in temperature compared to thermal polymerization. Again, most of photoinitiators may also decompose thermally, particularly at higher temperatures, the initiators may thus also undergo appreciable thermal decomposition in addition to photochemical decomposition. In such a case, both thermal and photochemical initiators must be taken into consideration. The activation energy values reported for the photopolymerization of acrylic monomers using various initiators are shown in Table 5.1.

5.5 Photopolymerization of acrylic monomers: Practice

5.5.1 UV curing and related processes

The UV curing of coatings and printing inks is based on the photoinitiation of radical and cationic polymerization. Photoinitiated radical polymerization of acrylate resins (monomers and oligomers) is widely employed commercially. Photogeneration of initiator radicals by α-cleavage or H abstraction is followed by reaction with the acrylate to produce a new radical that reacts with a second acrylate, etc.

$$I \xrightarrow{h\nu} I\bullet \qquad (48)$$

$$I\bullet + CH_2{=}CH\text{-}COOR \longrightarrow I\text{-}CH_2\text{-}CH^{\bullet}(COOR) \xrightarrow{CH_2{=}CH\text{-}COOR} \qquad (49)$$

$$I\text{-}CH_2\text{-}CH(COOR)\text{-}CH_2\text{-}CH^{\bullet}(COOR) \xrightarrow{CH_2{=}CH\text{-}COOR} \text{linear polymer} \qquad (50)$$

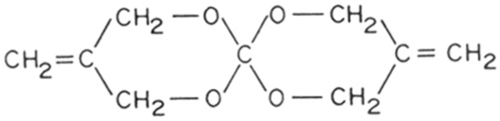
The utilization of monoacrylates yields a linear polymer. However, in UV curing a cross-linked polymer is produced from mixtures of mono-and multi-acrylates. The properties of the coatings such as hardness, flexibility, abrasion resistance, and solvent resistance, are determined by the composition of the acrylate resins. Low molecular weight acrylates, including monoacrylates, are required to adjust the viscosity of the coating, which is applied as a liquid usually without solvent. The design of acrylate resin systems for UV-curing applications and formulations has been the subject of many articles[4-7,49,50].

The advantages of UV curing over thermal curing include rapid network formation (in a fraction of a second by using high intensity light sources) and the utilization of heat-sensitive substrates. Most of the thermal energy, eg, from gas-fired ovens, is used to heat the substrate and volatilize the solvent necessary for application, whereas UV curing expends less energy. Solvent emissions are much lower, thereby reducing air pollution. In addition, UV curing requires less space.

Coatings and inks curable by UV are based on all substrates including glass, metal, paper, plastic, and wood. Specific applications include inks for lithographic, screen, flexographic, and letterpress printing; overprint varnishes; particle-board finishing; metal decoration; and vinyl flooring. Applications in the electronics industry, aside from photoimaging, include dielectric coatings, protective coatings for electrical components, conductive coatings, and coatings for optical fibers[51-53].

Rapid cure may lead to the development of stresses due to the inability of relaxation processes to keep pace with polymerization[54]. Shrinkage, which generally accompanies polymerization, contributes to stress formation. Shrinkages of 8-20% occur during polymerization of monofunctional acrylates and methacrylates[55] caused by the conversion of nonbonding distances between monomers to shorter bonding distances in polymers.

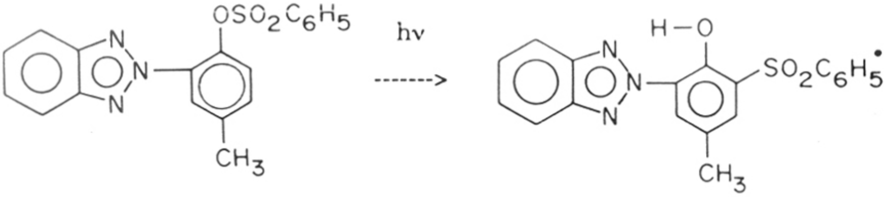
Small volume changes and even expansion may occur during polymerization of monomers that undergo ring-opening reactions as a consequence of bonding distances being converted into longer nonbonding distances in the ring-opening process. Expansion occurs during polymerization of the spiroorthocarbonate, that has been copolymerized by radical initiation with methacrylated resins in a composition for dental fillings[56]. The cured composition exhibits enhanced impact strength and abrasion resistance. Orthopedic devices[57] and dental materials[58] are cured with UV, particularly with photoinitiators for radical polymerization activated by visible light.



Spiroorthocarnonate

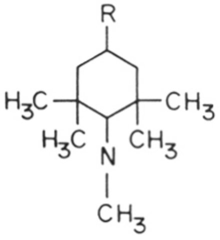
Photocurable compositions containing photoinitiators and functionality for both radical and cationic polymerization may provide greater flexibility in monomer and oligomer utilization, as well as improved film properties[59].

The limitations of UV-curing technology include the utilization of oddly shaped substrates and the curing of opaque coatings. Weatherability or durability requires special consideration, since conventional light stabilizers tend to interfere with the UV-curing process[60]. Latent light stabilizers activated by light absorption may alleviate this problem[61].



Latent light stabilizer   Active light stabilizer

The active light-stabilizer is generated in a gradient with the highest concentration at the air-coating interface where its presence is most desirable. Curing and light-stabilizer generation have to be carefully timed, since premature formation of the light stabilizer reduces the cure rate. Hindered amine light stabilizers which function primarily as antioxidants (qv), enhance the weatherability of UV-cured coatings[60].



Hindered amine light stabilizer

For curing opaque acrylate films, electron beams or curtains may be used, a process known as EB curing; UV and EB curing complement each other[5,62]. In the latter the depth of electron penetration is not limited by opacity, but is principally dependent on the density of the composition and may be controlled by accelerating voltage of the EB processor[63].

The rate of initiation for EB curing is expressed by Equation 52 in which I_e is the intensity of the electron beam, G is an efficiency factor, and M represents the monomer concentration[64]

$$R_i = I_e.G.M \qquad (52)$$

This may be compared to the initiation rate for UV curing.

An important distinction is that UV curing involves selective excitation of a guest, the photoinitiator, in the polymerizing media (host), whereas EB curing involves bulk excitation of the host.

A potential application for EB curing is the magnetic media market, including audio, video, and computer tapes, as well as rigid and floppy disks[65]. In applications where either UV or EB curing may be utilized, the substantially higher costs of the latter tend to favor the former, although lower maintenance costs for EB curing may tip the balance in its favor as volume output increases.

5.5.2 Photoimaging and Related Techniques

Photoimaging is based on exposure of a photopolymerizable system to light through a pattern of transparent and opaque regions, such as a photographic negative. Polymerization and cross-linking occur below the transparent regions, resulting in a latent image of insolubilized polymer in the exposed areas and soluble (uncross-linked) polymer in the unexposed areas. Development of the latent image may be accomplished by employing a solvent to dissolve the polymer in the unexposed areas selectively. The remaining cross-linked polymer serves as a barrier (or resist) against a subsequent process, such as etching or implantation.

The photopolymerizable system, which may contain photoinitiators, photocross-linking agents, or photocross-linkable polymers, is called a photoresist[52,53].

The process known as photolithography is used for integrated circuits (IC), printed circuits (PC), and printing plates[1,6,66]. Related technologies are electron-beam, x-ray, and ion-beam lithography, which utilize the corresponding resists.

The development of a printed circuit is shown in Figure 5.2. A copper laminated substrate (insulator) is coated with a photoresist and exposed to light through a photomask with transparent regions corresponding to the copper circuitry. The photoresist below the transparent regions is selectively cross-linked. The photomask is removed, the unexposed photoresist is selectively etched away below the unexposed regions. Removal of the cross-linked polymer yields the desired printed circuit. An excellent introduction to microlithography, the term used for fabrication of integrated (micro) circuits, includes physical and chemical aspects, as well as processing techniques[1].

Important parameters in photoimaging applications, particularly in IC fabrication, include resolution, sensitivity, and reproducibility (minimization of rejected devices). High resolution is desirable for high current density, which provides greater storage and faster processing of information on a computer chip, for example. Current photolithographic techniques reproduce features with dimensions of the order of 2-3μm utilizing near-UV light (360-410 nm). Figure 5.2 shows the development of a printed circuit by photolithography

Higher resolution is possible with shorter wavelength radiation, and photoresists currently being investigated are sensitive to mid UV (313 nm), deep UV (254 nm), and x-ray. Multilayer photoresists may also enhance the prospects for higher resolution[67]. Routine fabrication of IC devices with submicron features represents a major goal.

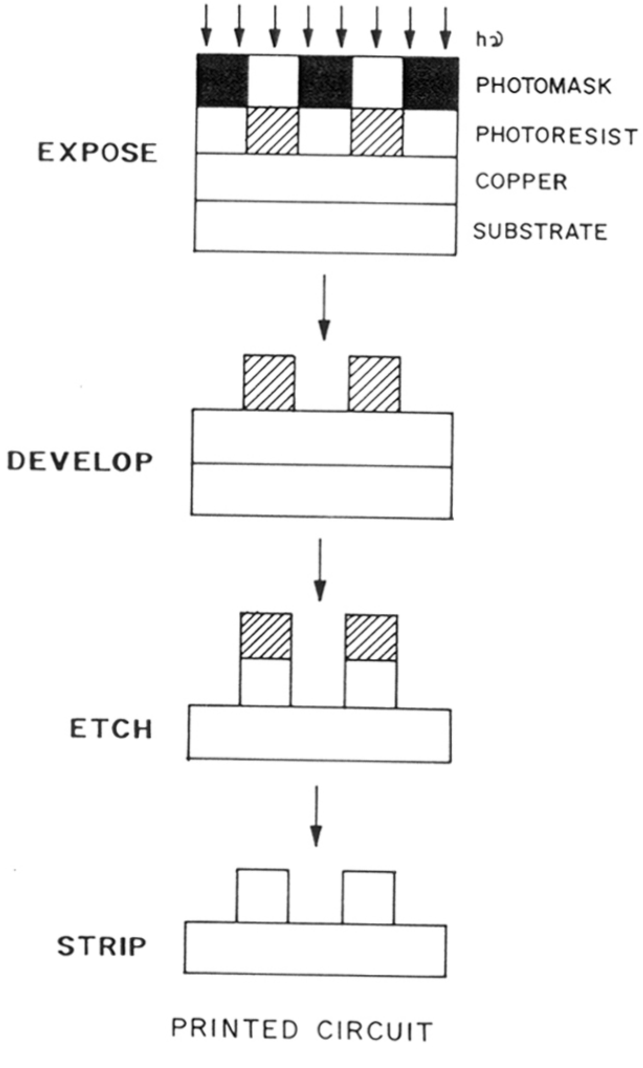


Fig. 5.2 Development of a printed circuit by photolithography

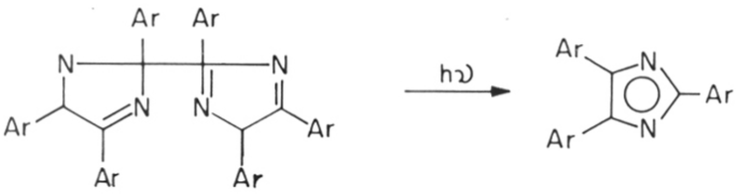
High sensitivity to radiation is desirable in order to achieve high volume throughput of devices. Photoresist sensitometry may be considered as the inherent photochemical efficiency Φ expressed by Equation 53, and as lithographic sensitivity, a measure of the photoefficiency of relief-image formation.

$$\Phi = \frac{\text{number of molecules reacted}}{\text{number of photons absorbed}} \qquad (53)$$

Lithographic sensitivity may be expressed as relative speed by exposure through a photographic-step tablet, with increasing absorbance by the tablet, i.e., decreasing light transmission[3,68]. Sensitivity may also be expressed in terms of the dose requirement, generally of the order of tenths to tens of mJ/cm^2. These values are useful only for comparison purposes[69].

Resolution requirements for printed circuits and printing plates are considerably less stringent (1-2 orders of magnitude) than for IC devices. Photoresist systems are employed in the manufacture of master printing plates[6,66], including typographic, lithographic, and intaglio plates for raised-image, planographic, and recessed-image printing, respectively.

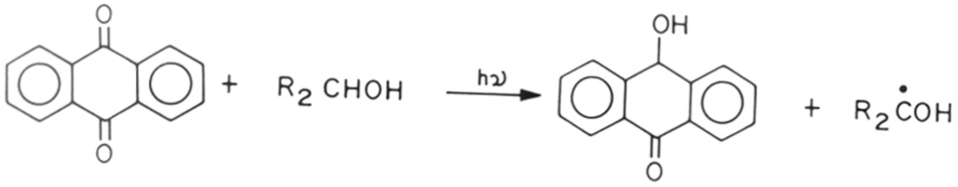
A photoresist system used in the fabrication of printed circuits is based on the photolytic cleavage of bisarylimidazoles into stable imidazoyl radicals. These radicals react with H donors, such as thiols (RSH), to yield thiyl radicals (RS.), which initiate polymerization of functional monomers, such as acrylated resins[70]. The spectral response of bisarylimidazoles may be extended deep into the visible region by photosensitization[71].



(54)

Photolytic cleavage of bisarylimidazoles

Printed circuits may also be fabricated by photometallization[72], where exposure through a photomask results in a latent image of metal clusters or nuclei in the exposed regions, which arise from reduction of metal ions by photogenerated radicals (R.).



(55)

$$2R^{\bullet} + Cu^{2+} \longrightarrow Cu^{0} + 2R^{-} \qquad (56)$$

The latent image is subsequently amplified to a printed circuit by electroless plating, which occurs only where catalytic sites, such as metal clusters, are present. A polymer-bound photoredox system may be included[73].

5.6 Objective in undertaking the present work

Organometallic compounds of Group IA and IIA initiate anionic polymerization of methyl methacrylate, whereas, the unstable compounds of Group IB and certain transition metals initiate free radical processes[74]. Contrary to earlier reports cited in patents[75], Minsker *et al.* reported that triisobutylaluminum polymerized methyl methacrylate at 60°C, but triethylaluminum failed to initiate the polymerization[76]. Allen and Casey[77,78] showed that photopolymerization of methyl methacrylate initiated by triethylaluminum occurs via 1:1 complex formation between methyl methacrylate and triethylaluminum by free radical mechanism where Wittig "ate" type complex was presumed to be the active initiator. Inoue and coworkers have extensively studied the light induced polymerization of methyl methacrylate using aluminum tetraphenylporphyrin as initiator[79]. This reaction proceeds by a concerted mechanism involving the enol ester of methyl methacrylate bound to aluminum as the active species, via nonradical intermediates. Recently Dimonie *et al.* reported the polymerization of methyl methacrylate at temperatures in the range of -78°C to 0°C using organoaluminum amides of the type $R_2AlNR'_2$ or $RAl(NR'_2)_2$[80]. An anionic-coordinative mechanism with aluminum amide enolates was proposed as propagating species. More recently Mardare *et al.* reported the polymerization of methyl methacrylate using aluminum derivatives of the type R_3Al or $RAl(NR'_2)_2$ complexed with a stable radical 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) in the presence of a bidentate Lewis base, 2,2'-dipyridyl (DPy). A radical mechanism involving the growing PMMA radicals reversibly stabilized by a neutral, tri or pentacoordinated Al derivative was proposed[81].

Methylaluminoxane, as discussed earlier in chapter I, is a product of controlled hydrolysis of trimethylaluminum and is believed to be a mixture of linear and cyclic oligomer of $[Al(CH_3)O]_n$ (n = 5-30) units[82]. On the basis of spectroscopic and X-ray crystallographic evidences of tert-butylaluminoxane Mason *et al.* have proposed that methylaluminoxane and related aluminoxanes have cluster type structures analogous to those found for the iminoalanes in which the aluminum centers are tetra-coordinate[83]. The importance of methylaluminoxane as a component of high activity homogeneous catalysis for olefin polymerizations is well understood[84]. However, its use in polymerization of acrylic ester monomers in presence of U.V. or visible light has not been reported so far.

The present work was undertaken to study the photopolymerization of methyl methacrylate using methylaluminoxane and trimethylaluminum as initiators.

5.7 References

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CHAPTER 6

PHOTOPOLYMERIZATION OF ACRYLIC MONOMERS INDUCED BY MAO AND TMA

6.1 Introduction

Vinyl polymerization can be initiated by ionic species as well as free radicals. Among the various polymerization methods for vinyl and related monomers, radical polymerization has been known for the longest time and is best understood. This method requires the introduction of a radical species into the monomeric system. The most common way of generating radicals is by homolytic decomposition of covalent bonds. This can be achieved by imparting enough energy to the bond, either by heating or by radiation. Photochemical reactions, either catalyzed or uncatalyzed, can also lead to initiation of free radical polymerization of vinyl and related monomers.

Photopolymerization, the utilization of electromagnetic radiation (or light) as the energy source for polymerization of functional monomers, oligomers, and polymers, is the basis of important commercial processes with broad applicability, including photoimaging[1-3], UV curing coatings[4-7] and inks[5-8]. These processes require that light is absorbed by the system and utilized to effect the formation of new chemical bonds. Photopolymerization may be achieved by the utilization of photoinitiators, photocross-linking agents, and photocross-linkable polymers. Photo-crosslinking agents and photocross-linkable polymers are used primarily in photoimaging applications and photoinitiators are more broadly used in both photoimaging and curing processes.

A variety of initiators are reported in the literature for the photopolymerization of acrylic monomers. The anionic polymerization of polar vinyl monomers especially acrylic and methacrylic esters is dominated by undesirable side reactions[9-11]. However, during the last decade, several initiating systems have been found for the preparation of acrylic polymers and block copolymers. A common feature of these systems is the presence of weakly electropositive elements (Al,Si) and their affinities towards the carbonyl oxygen atom, leading to metal enolates as propagating species. These initiators are known as silylketene acetals in group transfer polymerization[12,13], aluminum porphyrinates in "living" polymerization of (meth)acrylates[14,15], and organolanthanides in "living" polymerization of methyl methacrylate[16]. Minsker *et al.* reported that, triisobutylaluminum polymerized methyl methacrylate at 60°, but triethylaluminum failed to initiate the polymerization[17]. Allen and Casey[18,19] proved that the photopolymerization of methyl methacrylate initiated by triethylaluminum will occur via a 1:1 complex formation between methyl methacrylate and triethylaluminum by free radical mechanism where Wittig "ate" type complex is presumed to be the active initiator. On the contrary, Inoue and coworkers have studied the light induced polymerization of methyl methacrylate using aluminum tetraphenylporphyrin as initiator[20]. It was shown to proceed by a concerted mechanism involving the enol ester of methyl methacrylate bound to aluminum as the active species.

Methylaluminoxane as discussed earlier in chapter I, is a product of controlled hydrolysis of trimethylaluminum and has been believed to be a mixture of linear and cyclic oligomer of $[Al(CH_3)O]_n$ (n = 5-30) units[21]. On the basis of spectroscopic and X-ray crystallographic evidences of tert-butylaluminoxane, Mason *et al.* have proposed that methylaluminoxane and related aluminoxanes have cluster type structures analogous to those found for the iminoalanes in which the aluminum centers are tetra-coordinate[22]. The importance of methylaluminoxane as components of high activity homogeneous catalysts for olefin polymerizations is well understood[23].

Though the importance of methylaluminoxane in homogeneous Ziegler-Natta catalysis is well studied over the years, its use in polymerization of acrylic ester monomers like methyl methacrylate, methyl acrylate, butyl methacrylate etc., in presence of UV or visible light is not reported so far in literature.

Therefore a study of photopolymerization of acrylic ester monomers using methylaluminoxane (MAO) and trimethylaluminum (TMA) as photoinitiators was undertaken.

6.2 Experimental

All manipulations and operations were performed using standard benchtop inert atmosphere techniques using dry argon/nitrogen[24].

6.2.1 Materials

Acrylic monomers [methyl methacrylate (MMA), butyl methacrylate (BMA), and methyl acrylate (MA)] (Loba Chemie, Bombay) were purified by passing through a column of neutral alumina (Loba Chemie, Bombay) and then stirred over calcium hydride (Aldrich, USA) for 24 h and distilled under argon/nitrogen (<5 ppm moisture and <5 ppm oxygen, Industrial Oxygen Company Limited, Bombay) under reduced pressure prior to use. Sulphur free toluene and benzene (Loba Chemie, AR grade) were refluxed over sodium (Loba Chemie, Bombay) wire for 24 h and distilled under argon/nitrogen prior to use. Trimethylaluminum (TMA) and methylaluminoxane (MAO) (Schering - AG, Germany) were used as received. MAO (5.5 wt%, Average molecular weight = 850) in toluene had a methyl/aluminum content of 1.22. The content of free TMA in MAO was estimated by methyl/aluminum molar ratio and ^{1}H-NMR in toluene-d_8 independently and was found to be 12 (±1) mol%[25]. Hexaisobutyl dialuminoxane (HIBTAO, 4.3 wt% Al) and tetraisobutyl dialuminoxane (TIBDAO, 3.6 wt% Al) (Schering-AG, Germany) were used as received. Freshly distilled methanol (Loba Chemie, Bombay) was used as a non-solvent to precipitate the polymer.

6.2.2 Photopolymerization

Photopolymerizations were conducted in sealed glass tubes by illuminating the mixture of MMA/BMA/MA and MAO/TMA/TIBDAO/HIBTAO with UV radiation (350 nm) at 30°C in a Rayonet Photochemical reactor (The Southern New England Ultravoilet Co.,) for the desired time. Reactions were terminated by adding acidified methanol. The coagulated polymers were washed with excess of methanol and dried in vacuo to a constant weight at a temperature of 40°C.

6.2.3 Analysis

Aluminum content in MAO/TMA/TIBDAO/HIBTAO was estimated by EDTA titration. Methyl content in MAO was estimated by gas volume measurement of methane gas obtained on hydrolysis. NMR analysis of MAO and poly(methyl methacrylate) (PMMA) was performed in toluene-d_8 and $CDCl_3$, respectively, using a Bruker AC-200 spectrometer. UV analyses were performed on a Hitachi Model

220 UV-Visible spectrophotometer in toluene as solvent. The molecular weight distribution for the poly(methyl methacrylate) (0.3 % w/v in THF) was determined by using a Waters GPC - II equipped with a refractive index detector. The measurements were carried out using Waters μ - styragel columns (10^5, 10^4, 10^3, 500 Å) at ambient temperature (27°C) and THF as eluent at a flow rate of 1.0 mL/min. Monodisperse PMMA was used to calibrate the columns. Intrinsic viscosity of polymers were measured using an Ubbelhode viscometer using toluene or benzene as solvent at 30°C. For kinetic studies number average molecular weights of PMMA were calculated from the viscosity data determined in benzene by using the Equation 6.1[26].

$$[\eta] = 8.69 \times 10^{-5} \bar{M}n^{0.76} \qquad (6.1)$$

6.3 Results and Discussion

A 4:1 (mole ratio) mixture of MMA/MAO at room temperature shows a $\lambda_{max} = 284$ nm with a molar extinction coefficient of $\varepsilon = 0.435\ M^{-1}\ Cm^{-1}$ (Figure 6.1) The photopolymerization experiments were therefore conducted at 350 nm at 30°C. The results of the photopolymerization of acrylic monomers are discussed in the following sections.

6.3.1 Effect of catalyst concentrations, [MAO] on MMA photopolymerization

6.3.2 Effect of reaction time on photopolymerization of MMA initiated by MAO and TMA

6.3.3 Effect of TMA in MAO on photopolymerization of MMA

6.3.4 Effect of nature of aluminoxane on photopolymerization of MMA

6.3.5 Photopolymerization of acrylic monomers induced MAO: A comparison

6.3.6 Kinetics of MMA photopolymerization initiated by MAO and TMA

6.3.7 Mechanism of photopolymerization of MMA induced by TMA and MAO

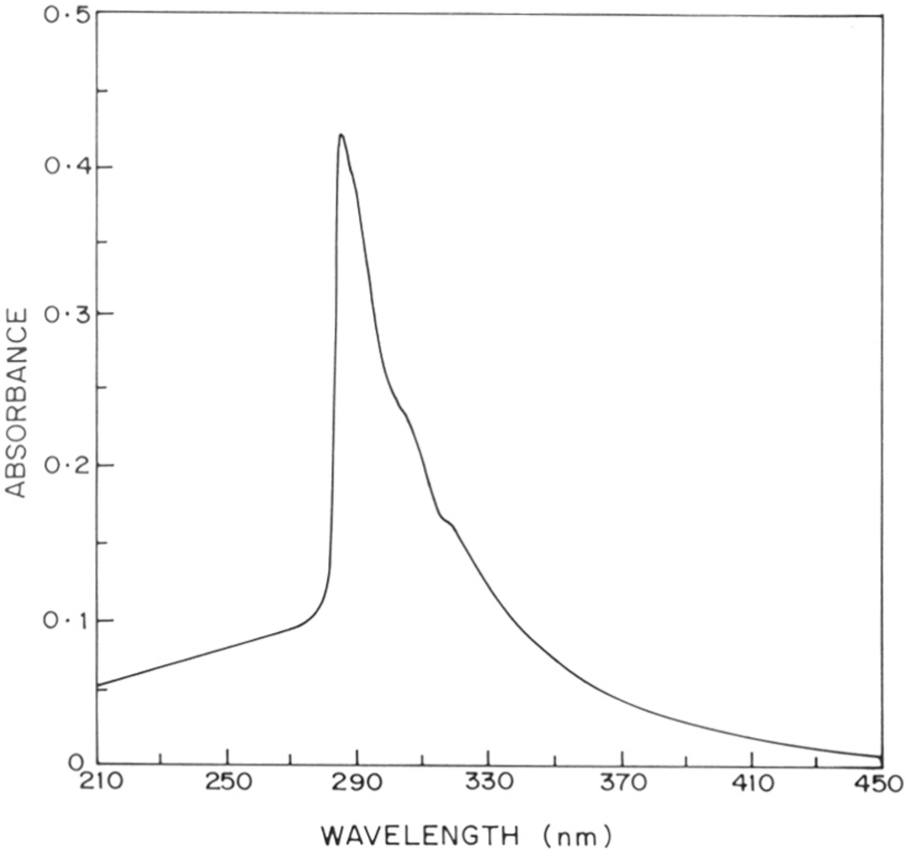


Fig. 6.1 UV absorption spectrum of 4:1 (mol ratio) mixture of MMA and MAO

6.3.1 Effect of catalyst concentration, [MAO] on MMA photopolymerization

It was confirmed that in the absence of light MAO failed to polymerize MMA. Photopolymerization of MMA was conducted in bulk with MMA/Al mole ratios of 70, 106, and 212 at MAO concentration of 13.4 x 10^{-2}, 8.8 x 10^{-2} and 4.4 x 10^{-2} mol/L respectively at 30°C for 4 h. The results are shown in Table 6.1. Conversions were found to be higher at high MAO concentration i.e., lower MMA/Al mole ratios. Molecular weights were also found to be higher at lower MMA/Al ratios.

6.3.2 Effect of reaction time on photopolymerization of MMA initiated by MAO and TMA

Photopolymerization of MMA was conducted in bulk at MMA/Al mole ratios of 70 at a concentration of 13.4 x 10^{-2} mol/L of MAO (by aluminum) at 30°C. Photopolymerization of MMA induced by MAO and TMA was studied as a function of time. The results are shown in Table 6.2. A plot of conversion and number-average molecular weight as a function of time is shown in Figure 6.2. With MAO both conversion and molecular weight increased linearly with time. The plot of number-average molecular weight vs conversion was also linear (Figure 6.3). The behavior is reminiscent of the "living" radical polymerization of MMA observed with thermal iniferters and photoiniferters[27]. However, compared to thermal iniferter induced and photoiniferter initiated polymerizations higher conversions were obtained in shorter reaction times. The molecular weights of poly(methyl methacrylate)s were also substantially higher. Molecular weights achieved in the case of MAO-induced photopolymerization of MMA were much higher than those obtained through TMA-induced photopolymerization. The molecular weight distribution for MAO- induced polymerization was found to be in the range of 1.5 - 1.7. No broadening of the distribution was observed with increase in conversion (Fig 6.4).

Table 6.1 Photopolymerization of MMA Using MAO as Initiator[a]

S. No.	[Al].10^2 (mol/L)	[MMA]/[Al]	Time (min)	Conversion (%)	$[\eta]^b$ (dL/g)
1.	4.4	212	240	20	1.22
2.	8.8	106	240	24	1.32
3.	13.4	70	240	36	1.66

[a] Polymerization conditions: MMA = 4.68 g, temperature = 30°C, [b] In toluene at 30°C

Table 6.2 Photopolymerization of MMA Using Organoaluminums as Photoinitiators[a]

S. No.	Organoaluminum compound	Time (min)	Covnersion (%)	[η][b] (dL/g)	$\bar{M}$w. 10^{-5}	$\bar{M}$n. 10^{-5}	$\bar{M}$w/$\bar{M}$n	% triads		
								mr	rr	mm
1.	MAO	45	7	0.83	4.26	2.63	1.62	39	55	6
2.	MAO	120	12	0.94	4.84	3.14	1.54	34	60	6
3.	MAO	240	36	1.66	8.33	4.95	1.68	33	63	4
4.	MAO	360	51	2.20	13.20	8.77	1.50	35	58	7
5.	TMA	45	30	0.27	1.07	0.54	-1.98	37	51	12
6.	TMA	70	62	0.34	-	-	-	35	54	11
7.	TMA	120	80	0.37	1.71	1.05	1.62	38	50	12
8.	TMA	180	85	0.36	1.67	0.98	1.70	34	48	18

[a] Polymerization conditions: MMA = 4.68 g, temperature = 30°C, [Al] = 13.4×10^{-2} mol/L, [MMA]/[Al] = 70

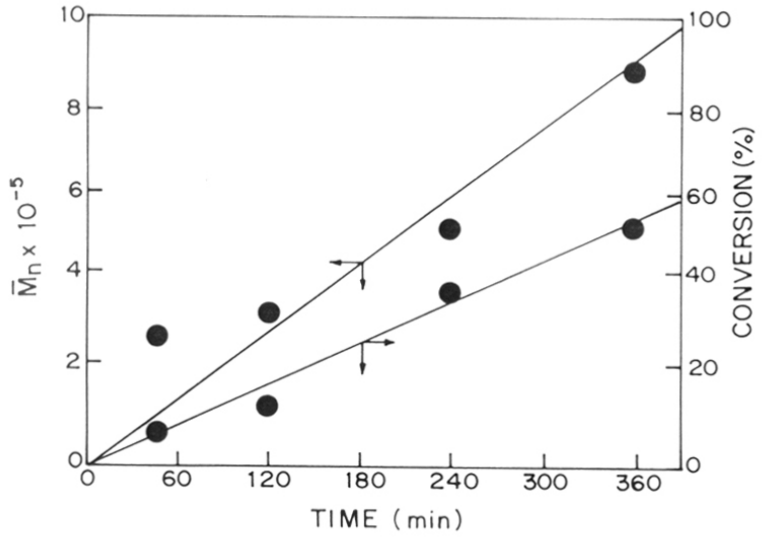


Fig. 6.2 Plot of $\bar{M}n$ and conversion with time for the photopolymerization of MMA with MAO

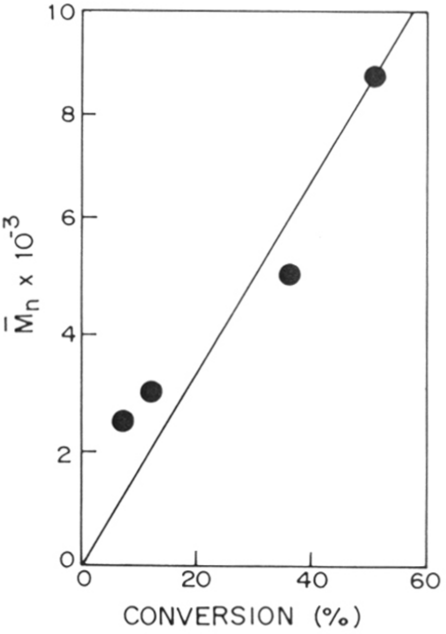


Fig. 6.3 Plot of $\bar{M}n$ vs conversion for the photopolymerization of MMA with MAO

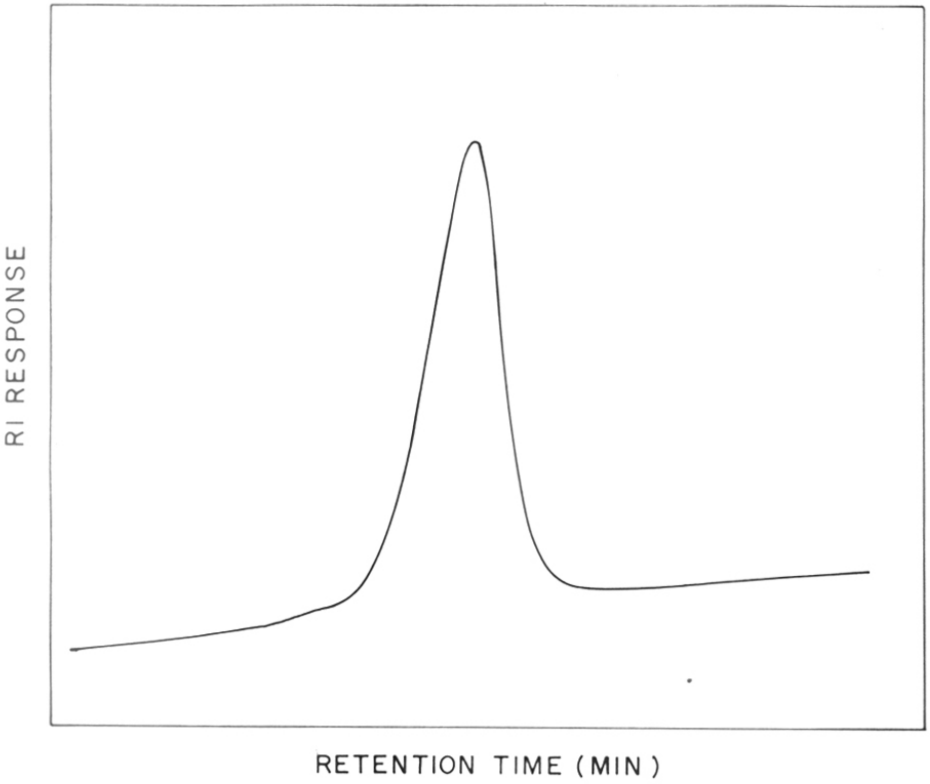


Fig. 6.4 Gel Permeation Chromatogram of poly(methyl methacrylate)

6.3.3 Effect of TMA in MAO on photopolymerization of MMA

As discussed earlier, MAO is synthesized by partial and controlled hydrolysis of TMA. MAO thus synthesized always contains residual TMA (complexed or free) which cannot be removed completely[28]. Photopolymerization of MMA was conducted in bulk with 7.8, 10 and 15 mol% of TMA in MAO at 30°C. The mol% TMA in MAO was maintained by removing excess TMA from MAO by applying vacuum (for low mol% TMA) or by adding TMA externally (for high mol% TMA). The results are shown in Table 6.3 and graphically plotted in Figure 6.5. With increase in mol% of TMA the conversion is found to be increasing linearly passing through the origin. This indicates that the actual initiating species must be residual TMA present in MAO.

6.3.4 Effect of nature of aluminoxane on photopolymerization of MMA

Photopolymerization of MMA was performed in bulk using three different aluminoxanes, namely, MAO, TIBDAO and HIBTAO at a aluminum concentration and MMA/Al ratio of 8.8×10^{-2} mol/L and 106 respectively at 30°C for 4 h. The results are shown in Table 6.4. Molecular weights were found to be similar in all the polymerizations initiated by MAO, TIBDAO and HIBTAO. Conversions for HIBTAO and TIBDAO initiated polymerizations were found to be the same (20%) and slightly higher conversion (24%) was observed in the case of MAO initiated polymerizations. This may be due to the high reactivity of residual TMA present in MAO compared to residual triisiobutylaluminum (TIBAL) present in TIBDAO and HIBTAO.

6.3.5 Photopolymerization of acrylic monomers induced by MAO: A comparison

Photopolymerization of MA, MMA and BMA were performed by using MAO as photoinitiator. MAO 0.068 mol/L (as aluminum) and monomer 11.68 mol/L were employed for polymerization at 30°C for 2 h. The results are shown in Table 6.5. Conversion for MA, MMA and BMA were found to be 93, 7.5 and 6.7% respectively. Poly(methyl acrylate) was found to be insoluble in all common solvents such as

Table 6.3 Effect of TMA in MAO on Photopolymerization of MMA[a]

S. No.	% TMA in MAO	Conversion (%)
1.	7.8	1.7
2.	10	2.4
3.	15	5.0

[a] Polymerization conditions : MMA = 4.68 g, temperature = 30°C, [MMA]/[Al] = 70, time = 30 min

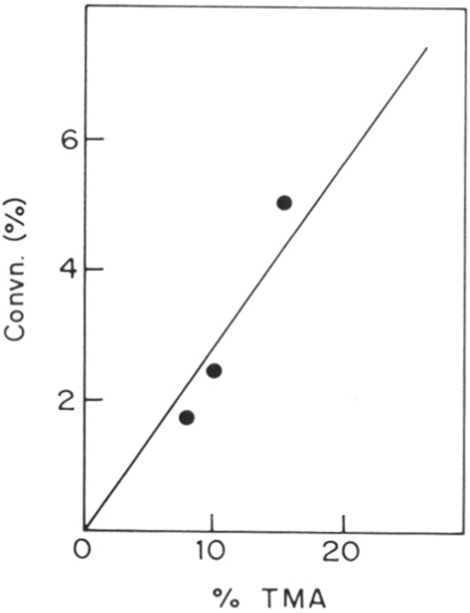


Fig. 6.5 Plot of conversion vs mol% TMA present along with MAO for the photopolymerization of MMA with MAO

Table 6.4 **Effect of Nature of Aluminoxane on Photopolymerization of MMA**[a]

S. No.	Organoaluminum Compound	Conversion (%)	$[\eta]^b$ (dL/g)
1.	MAO	24	1.32
2.	HIBTAO	20	1.29
3.	TIBDAO	20	1.30

[a] Polymerization conditions: MMA = 4.68 g, temperature = 30°C, [Al] = 0.088 mol/L, [MMA]/[Al] = 106, time = 240 min, [b] in toluene at 30°C

Table 6.5 Photopolymerization of Acrylic Monomers Induced by MAO: A Comparison

S. No.	Monomer	Time (min)	Conversion (%)	$[\eta]^e$ (dL/g)
1.	Methyl acrylate^a	120	93.0	b
2.	Methyl methacrylate^a	120	7.5	3.3^c
3.	Butyl methacrylate^a	120	6.7	6.2^c
4.	Butyl methacrylate^d	60	9.91	1.6^e
5.	Butyl methacrylate^d	120	15.5	2.0^e
6.	Butyl methacrylate^d	180	22.1	2.0^e
7.	Butyl methacrylate^d	240	30.0	2.0^e

[a] Polymerization conditions: Monomer = 11.675 mol/L, Al = 0.068075 mol/L, Temperature = 30°C; [b] Polymer was found to be insoluble in toluene and benzene; [c] Intrinsic viscosity determined in toluene 30°C; [d] Polymerization conditions: BMA = 6.286 mol/L, Al = 0.0898 mol/L, Temperature = 30°C; [e] Intrinsic viscosity determined in benzene at 30°C

toluene and benzene. This is possibly due to crosslinking in poly(methyl acrylate). Chain transfer to polymer is a distinct possibility especially at such high conversions. The molecular weight of polymer derived from BMA was higher compared to that derived from MMA ([η] 6.2 and 3.3 respectively). MA was more reactive when compared to MMA and BMA. This is attributed to lower steric hindrance and the absence of alkyl group in the α position.

Photopolymerization of BMA was performed in bulk at BMA/Al ratio of 70 [BMA = 6.286 mol/L, MAO = 0.0898 mol/L (as aluminum)] at 30°C as a function of time. The results are shown in Table 6.6. For 1,2,3 and 4 hours the viscosities of the poly(butyl methacrylate) were found to be 1.6, 2.0, 2.0 and 2.0 respectively. This behavior is different from that observed with MMA.

6.3.6 Kinetics of MMA photopolymerization

All kinetic studies were performed at <10% conversion.

6.3.6.1 Initiator exponent

The results of photopolymerization of MMA at 30°C using different [MAO] and [TMA] 0.05 to 0.27 and 0.06 to 0.30 mol/L (as Al) respectively are presented in Table 6.6. Rates of polymerization (Rp) were calculated from the yield of the polymer.

Figure 6.6 shows a plot of log Rp vs log [MAO] and log Rp vs [TMA]. From the slopes of the plots initiator exponent values are found to be 0.76 and 0.40 for MAO and TMA initiators respectively.

6.3.6.2 k_p^2/k_t value

The kinetic parameter k_p^2/k_t at 30°C for the photopolymerization of MMA was evaluated from the plot (Figure 6.7) of $1/\bar{P}n$ vs $Rp/[M]^2$ over low Rp range using data given in the Table 6.6, following usual procedures and in accordance with the following simplified form of Mayo Equation 6.1[29]

Table 6.6 Photopolymerization of MMA Using Organoaluminum Compounds as Photoinitiators[a]

S. No.	Initiator	[Al] (mol/L)	[MMA]/[Al]	Conversion (%)	$[\eta]^b$ (dL/g)	Mn. 10^{-5}	$\bar{P}n$	Rp.10^{-4} (M/Sec)	Initiator exponent	$K_p^2/K_t \cdot 10^{-2}$ (Lit. mol^{-1}. Sec)
1.	TMA	0.0608	124	4.82	0.67	1.30	1295	1.01	0.40	0.2
2.	TMA	0.1216	62	4.57	0.57	1.06	1061	0.96		
3.	TMA	0.1825	41	5.33	0.54	0.99	985	1.12		
4.	TMA	0.2027	37	6.12	0.44	0.74	742	1.28		
5.	TMA	0.2433	31	5.40	0.46	0.80	800	1.13		
6.	TMA	0.3041	25	6.40	0.41	0.67	670	1.34		
7.	MAO	0.0514	138	2.40	1.49	3.73	3720	0.47	0.76	4.0
8.	MAO	0.1028	69	3.44	1.27	3.17	3162	0.69		
9.	MAO	0.1542	46	5.86	1.17	2.93	2926	1.15		
10.	MAO	0.1885	38	6.65	1.21	3.04	3031	1.31		
11.	MAO	0.2227	32	7.05	1.14	2.85	2849	1.39		
12.	MAO	0.2741	26	7.86	1.06	2.66	2655	1.55		

[a] Polymerization conditions: Temperature = 30°C, Time = 20 min in the case of TMA initiated and 60 min in the case of MAO initiated polymerizations;
[b] Intrinsic viscosity determined in benzene at 30°C

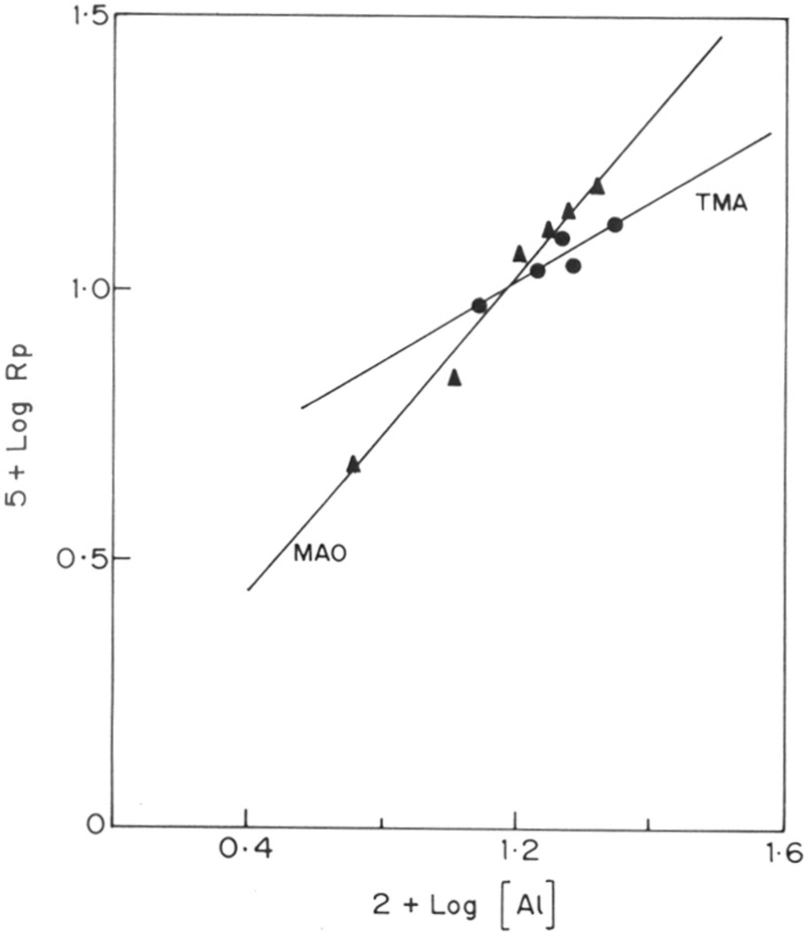


Fig. 6.6 Plot of log Rp vs log [Al] for the photopolymerization of MMA with TMA and MAO initiators independently

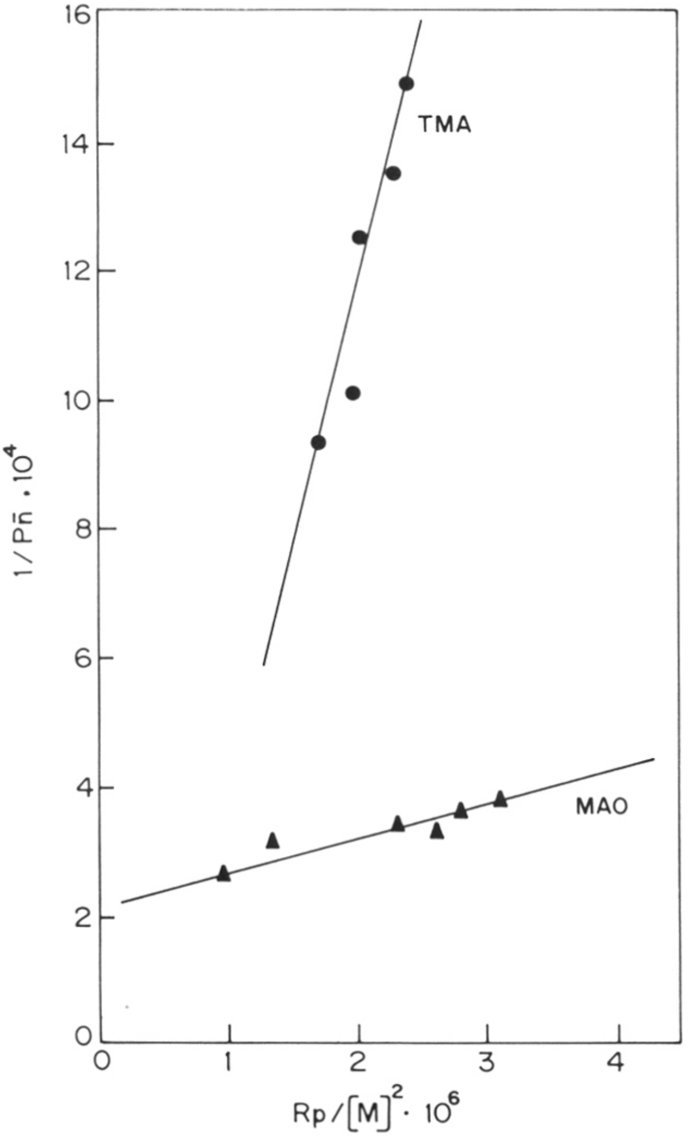


Fig. 6.7 Plot of $1/\bar{P}n$ vs $Rp/[M]^2$ for the photopolymerization of MMA with TMA and MAO initiators independently

$1/\bar{P}n = 1.85 (k_t/k_p^2) (Rp/[M]^2) + C_M + C_I ([I]/[M])$ (6.2)

where, k_p and k_t are rate constants for propagation and termination reactions respectively; [M] and [I] stands for monomer and initiator concentrations respectively. C_M and C_I stand for chain transfer constant to monomer and initiator respectively.

$\bar{P}n$ was calculated from $\bar{M}n$ which in turn was calculated by using Equation (6.1) from the viscosity of the polymer determined in benzene at 30°C.

It is assumed that chain transfer reactions with monomer and initiator would not affect the slope of the plot in Figure 6.7 and the calculated k_p^2/k_t values for MAO and TMA are 0.04 and 0.002 Lit.mol^{-1}.sec respectively. These k_p^2/k_t values are in good agreement with some of the reported values in the literature for the polymerization of MMA (See chapter V Table 5.1). The k_p^2/k_t values calculated for these experiments should be taken as an approximate because it is assumed in the calculation that any perturbation of the termination process from the usual bimolecular mechanism will not appreciably affect the slope of the plot in Figure 6.7. The k_p^2/k_t value for MAO initiated polymerization of MMA is around twenty times higher than that of TMA. This can be ascribed to either higher propagation rate in case of MAO induced photopolymerization or lower rate of chain termination by recombination.

6.3.7 Mechanism of photopolymerization of MMA induced by TMA and MAO

The following experimental evidences support the hypothesis that the propagating species is a free radical.

1. In presence of hydroquinone the polymerization process is inhibited for both MAO and TMA initiated polymerizations. In case of MAO initiated polymerization (reaction conditions = [Al] = 13.4 x 10^{-2} mol/L, MMA/Al = 70, Time = 240 min) conversion decreased from 36% (without hydroquinone) to 4% (with 1 mol% hydroquinone based on MMA). In the case of TMA initiated

polymerization (reaction conditions = [Al] = 13.4 x 10^{-2} mol/L, MMA/Al = 70) conversion decreased from 85% (without hydroquinone, 2 h) to 14% (with 1 mol% hydroquinone based on MMA, 4 h)

2. The initiator exponent and k_p^2/k_t values are in the range of values reported for free radical photopolymerization of MMA.
3. ^{1}H-NMR of PMMA shows the characteristic fractions for chain end free radical as the propagating species[30] (Figure 6.8, Table 6.2).
4. The molecular weight distribution of PMMAs obtained were in the range of 1.5 to 1.7. This indicates that the predominant chain breaking event is termination by coupling.

However, there are major differences between conventional free radical initiated polymerization and photopolymerization initiated by MAO. These are (a) a linear increase of $\overline{M}n$ with conversion and time (b) ability to produce substantially higher molecular weight PMMA's compared to TMA initiated MMA photopolymerization. These features resemble the well studied free radical polymerization using thermal and photo-iniferters[31]. However, unlike the recently reported living free radical polymerizations[32-34] MAO induced photopolymerization do not show living radical polymerization behavior. This is indicated by the finite k_p^2/k_t values and polydispersities > 1.5.

Nevertheless, experimental evidence indicates that the radical chain ends exhibits unusual stability. For a given monomer at a given temperature, the average length of the kinetic chain depends primarily on the value of k_p^2/k_t. For MMA bulk polymerization with typical k_p^2/k_t value of 0.03 at 60°C, the theoretical upper limit of attainable molecular weight can be estimated to be about a million[35]. It is interesting to note that in the photopolymerization of MMA, with a k_p^2/k_t value of 0.04, the observed $\overline{M}n$ is 877,000(entry 4, Table 6.2). This indicates that in case of MAO induced photopolymerization of MMA, the theoretical limit of molecular weights is being reached. One can therefore infer that under these conditions close to one polymer molecule is being produced by one kinetic chain.

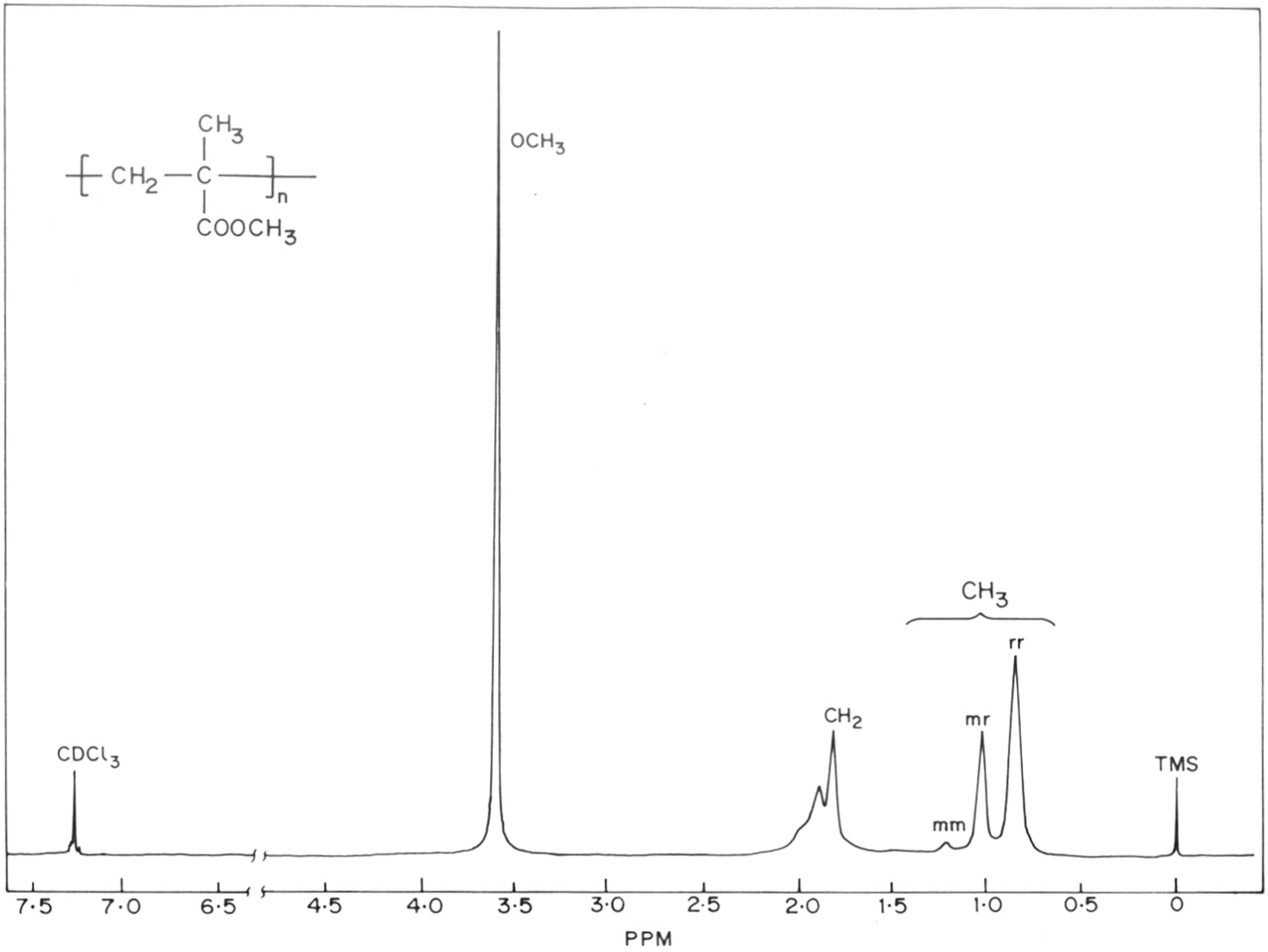


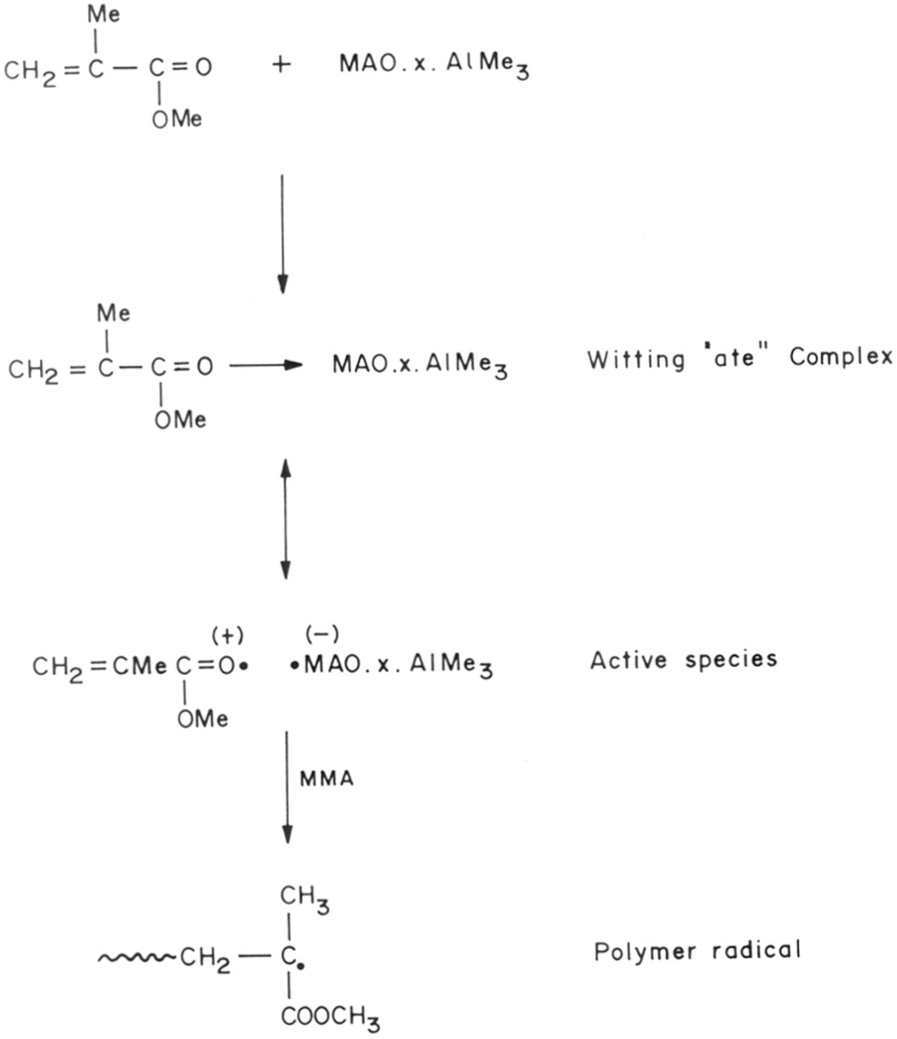
Fig. 6.8 200 MHz ^{1}H-NMR spectrum of poly(methyl methacrylate) in $CDCl_3$ with TMS as internal standard

The reasons for the unusual stability of the propagating free radical must be sought in the structure of MAO. It is quite clear from the experimental evidence that the free radicals are generated by the photodecomposition of the "ate" complex involving TMA (Scheme 6.1). We propose that the free radical is trapped in the "cage" like structure of MAO (Figure 6.9b) conferring on it a high degree of stability and consequent reduction in the rate of termination by recombination.

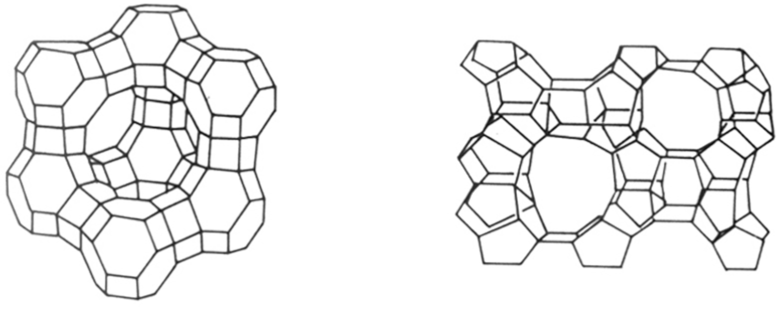
These cages, consisting of Al-O-Al linkages, are similar to other three dimensional structures such as, zeolites or γ-Al_2O_3. Unusual behavior of free radicals within such cage like cavities of zeolites and γ-Al_2O_3 are well documented in the literature[36-39]. In the decomposition of dimethyl 2,2'-azodiisobutyrate Tanaka[40] *et al.* and Tanaka[41] reported a long lived polymer radical (PMMA) in presence of the silica gel and zeolites (pore size 70 Å) which subsequently resulted in the polymer. The polymer radical was observed even after a long period of darkness (1.5 h). This was attributed to the diffusion or the suppression of the mobility of the propagating radical leading to the retardation of the termination reaction. It was shown that in large pores (zeolites and silica gel) diffusion of the monomer becomes easy, whereas mobility of a polymer radical is restricted, consequently a monomer is converted into a polymer at relatively high rate to give a long lived polymer radical. In another study methyl methacrylate radical was shown to be stable even at 140°C in the presence of zeolites for 1 h[42].

The unusual stability of free radicals within zeolite cages has been explained by Ramamurthy[36,37] et al. The zeolite cages provide electronic as well as steric requirements for a comfortable stabilization of the freeradicals. Thus, a suitable host (zeolite) - guest (radical) relationship with a tight-fitting arrangement between the two provides long life to the radical. The unique steric and electrostatic effects of zeolite cages help stabilize the unstable transcient species by retarding the back electron transfer as compared to those in solution[39].

Based on spectroscopic and single crystal X-ray studies, on tert-butylaluminoxane, Mason[29] *et al.* have advanced a cluster structure for aluminoxane (Figures 6.9a and 6.9b depict the situation pictorially for zeolite and aluminoxane). Their studies suggest a similar structure with tetra coordinate aluminum for MAO, as against



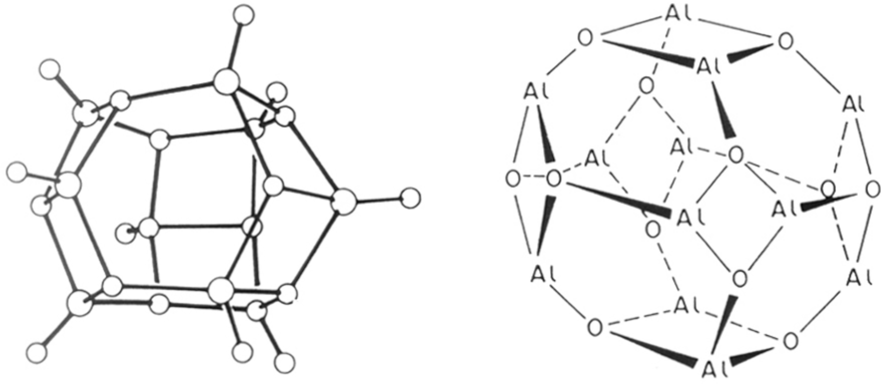
Scheme 6.1 Mechanism of photopolymerization of MMA using MAO initiator



ZEOLITE-X,Y

ZSM-5

Fig. 6.9a Zeolite structure



Molecular structure of tert-butylaluminoxane $[(^{t}\text{Bu})\text{Al}(\mu_3\text{-O})]_9$. Methyl groups are omitted for clarity

Plausible molecular structure of tert-butylaluminoxane $[(^{t}\text{Bu})\text{Al}(\mu_3\text{-O})]_{12}$. ^{t}Butyl groups are omitted for clarity

Fig. 6.9b Cage like structure of aluminoxane hitherto accepted straight chain or cyclic nature, involving aluminum with a coordination number of three. Thus there appears to be striking similarity between the structure of MAO and zeolites.

It is, therefore, conceivable that MAO also stabilizes the acrylate radical in a manner similar to zeolites. Thus, the MAO cluster acts as a good host to accommodate and stabilize the acrylate guest radical.

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CHAPTER 7

SUMMARY AND CONCLUSIONS

PART - A

Ethylene polymerization studies using Cp_2ZrCl_2-MAO/TIBDAO/ $AlMe(BHT)_2$ catalysts

Synthesis of MAO has been systematically studied by varying the reaction time and temperature at a TMA:H_2O ratio of 1:2. Synthesized MAOs have been characterized by ^1H NMR, methyl/aluminum molar ratio and cryoscopy. (MAO I: methyl/aluminum molar ratio = 2.2, average molecular weight = 420; MAO II: methyl/aluminum molar ratio = 1.75, average molecular weight = 590, MAO III: methyl/aluminum molar ratio = 1.65, average molecular weight = 805) These MAOs have been used as cocatalysts along with Cp_2ZrCl_2 for the polymerization of ethylene at one atmosphere pressure and 70°C at Al/Zr mol ratio of 100000 ($[Zr] = 8.8 \times 10^{-7}$ mol/L). In the case of MAO I, the observed Rp versus time curve is reminiscent of simple TMA cocatalyzed polymerization, whereas, MAO III showed a decay type kinetic profile similar to MAO obtained commercially. MAO II shows an intermediate behavior. Intrinsic viscosity of poly(ethylene)s obtained using MAO I, II and III increases from 1.1 to 3.1. Thus catalyst activity as well as molecular weight of poly(ethylene) increases with increase in MAO molecular weight.

$AlMe(BHT)_2$ has been synthesized and characterized by melting point, ^1H NMR, mass spectroscopy and cryoscopy techniques. $AlMe(BHT)_2$ has been found to be inactive for the polymerization of ethylene along with Cp_2ZrCl_2. However, addition of TMA to Cp_2ZrCl_2-$AlMe(BHT)_2$ catalyst system produces a catalyst of marginal activity with a kinetic profile similar to that of Cp_2ZrCl_2-MAO system.

It has also been found that improved catalyst activities, high rate of polymerization and molecular weights can be achieved at lower Cp_2ZrCl_2 concentration and high Al/Zr mol ratios. At lower temperature of polymerization molecular weight increases but catalytic activity decreases.

The studies also reveal that the addition of TMA to Cp_2ZrCl_2-MAO catalyst system causes a significant increase in catalyst activity as well as extending the kinetic life time of the catalyst. A small reduction in Rp(max) is also observed. Also addition of TMA causes the kinetic profile changes from a decay type to a buildup type curve. Interestingly and contrary to data published in prior literature, molecular weight of poly(ethylene) is only marginally depressed by addition of free TMA to MAO.

The catalyst system Cp_2ZrCl_2-TIBDAO exhibits a behavior similar to Cp_2ZrCl_2-MAO system for ethylene polymerization at one atmosphere pressure and 70°C but with lower catalyst activity and rate of polymerization.

The present studies establish that the average degree of oligomerization of MAO should be at least 13 corresponding to a molecular weight of 800 for achieving optimum activity. A methyl/aluminum mol ratio of 1.6 and free TMA content of 30 mol% also appear necessary for the system to exhibit an optimum efficiency.

These results again testify to the unique role played by MAO in the metallocene catalyzed polymerization of ethylene. The high activity of the catalyst appear to be a consequence of the extraordinary stability conferred by MAO on the catalytically active cationic zirconium centers. This must be due to the unique cluster type structures of MAO oligomers with well defined cages containing six, nine or twelve aluminum atoms. Presence of some free TMA is essential for high activity. TMA presumably plays multiple roles in these polymerization. It alkylates the metal-halogen bond, acts as a scavenger of adventitious impurities and suppresses deactivation of catalyst by suppressing the side reaction of catalyst component leading to a Zr-C-Al bond, through a transmetallation reaction.

Thus the high activities observed for Cp_2ZrCl_2-MAO catalysts is due to a combination of factors, namely, the unique cage like structures of MAO oligomers and the ability of associated TMA to act as a good alkylating and transmetallating agent of the transition metal and preventing deactivation of the active center.

PART - B

Photopolymerization of acrylic monomers induced by methylaluminoxane and trimethylaluminum

MAO has been found to initiate the photopolymerization of acrylic monomers with some interesting features. MAO initiated photopolymerization exhibits a linear increase of both conversion and number average molecular weight with time. This behavior is reminiscent of the "living" radical polymerization of MMA observed with thermal iniferters and photoiniferters. Kinetic features of MAO initiated photopolymerization of MMA are significantly different from that of TMA. k_p^2/k_t and initiator exponent values for MAO and TMA initiated photopolymerization of MMA have been found to be 0.04, 0.002 Lit.mol^{-1}.sec and 0.76 and 0.40 respectively. In case of MAO initiated photopolymerizations it has been established that the actual initiating species is the residual TMA present in MAO. Experimental evidences have been provided to conclude that the mechanism of photopolymerization of MMA is a free radical process. Presumably Wittig "ate" type of complex acts as the initiating species. All evidences thus point out to the unusual stability of the growing free radical in presence of MAO. It is proposed that the growing radical is trapped within the cages of the MAO oligomer clusters. These cages, consisting of Al-O-Al bonds, are similar to other three dimensional structures such as, zeolites and γ-Al_2O_3. Unusual behavior of free radicals within such cage-like cavities of zeolites and γ-Al_2O_3 are well documented in the literature.

In conclusion, the results presented in this thesis attest to the remarkable role played by oligomeric aluminoxanes in stabilizing both cationic and radical intermediates. The unusual stability of the electrophilic cationic zirconium species and that of a growing free radical, responsible for efficient polymerization of ethylene (by coordination mechanism) and methyl methacrylate (by radical mechanism) respectively must be related to the unique structural features of oligomeric aluminoxanes. Presumably, the cage like structures, consisting of Al-O-Al bonds, trap these reactive intermediates as guest-host complexes. The interior cavities of such cages must offer an environment capable of stabilizing both the cationic metal species or a carbon free radical.

SCOPE FOR FUTURE WORK

Synthesis of MAO

Additional studies are required to further clarify the role of MAO properties on polymerization activity. Towards this end further studies are required with regard to variables such as reaction temperature, water/TMA ratio and reaction time. Also, a comparative study of crystal water and free water method would be desirable. Other hydrated salts (eg. $MgCl_2.6H_2O$, prehydrated silica) needs to be tried. These methods may lead to formation of MAO supported on $MgCl_2$ or silica which are interesting precursors for supported metallocene-MAO catalysts.

Polymerization using MAO/Cp_2MCl_2

Further studies are needed to unequivocally establish the role of TMA in stabilizing the active center. It will be useful to study the rate of methane evolution by reaction of MAO with Cp_2ZrCl_2 in presence of varying amounts of TMA and observe whether there is a suppression of methane evolution. Additional studies on ethylene polymerization needs to be conducted using MAO containing free TMA, left behind from synthesis and TMA added to MAO, after freeing MAO of all TMA left behind during the synthesis.

Photopolymerization of MMA induced by MAO

Unambiguous evidence for long lived radicals needs to be established by ESR. Also, ability of the growing PMMA radicals to initiate block copolymerization needs to be explored. It will be useful to explore a series of alkylacrylates, e.g., methyl methacrylate, butyl methacrylate, t-butyl methacrylate for establishing the role of steric effects on the photopolymerizability behavior. Nitrile bearing monomers, methacrylonitrile is also worthy of study.

APPENDIX

POLYMERIZATION OF STYRENE USING TITANIUM-n-BUTOXIDE-AlMe(BHT)$_2$ CATALYST

A.1 Introduction

Poly(styrene) is one of the few polymers which can be produced by free radical, cationic, anionic and coordinative polymerization. In commercial practice, free radical polymerization of styrene is predominantly used for the production of homopolymers[1] whereas, anionic polymerization is employed for the production of block copolymers[2].

Poly(styrene) can exist in three forms, namely, atactic, isotactic and syndiotactic. Poly(styrene) produced by free radical and cationic polymerization is nonstereospecific. The concentration of triads, namely mm, mr and rr, are 10, 15 and 75% respectively for poly(styrene) obtained by free radical polymerization and 30, 20 and 50% in the case of the product obtained through cationic polymerization[3]. Poly(styrene) prepared with anionic initiators is also reported to be non-stereospecific with a value of mr triad 56%[4]. On the contrary, Ziegler-Natta catalysts based on hologenated compounds of transition metals, either as such or supported on magnesium halides, in combination with alkylaluminums, with electron donors produce predominantly isotactic polymers[5].

However, syndiotactic poly(styrene) with a high degree of stereoregularity was unknown till recently. In 1986, Ishihara *et al.* reported the first example of syndiotactic poly(styrene) with 94% racemic heptad configuration produced using a novel catalyst system containing a titanium compound and an organoaluminum compound[6]. Since this seminal discovery, synthesis of syndiotactic poly(styrene) using homogeneous Ziegler-Natta catalysts has attracted considerable attention.

Some distinct characteristics of atactic, isotactic and syndiotactic poly(styrene) are shown in Table A.1. Atactic poly(styrene) is amorphous in nature. The use of this amorphous polymer is limited by its low glass transition temperature (Tg) of about 100°C. Above this temperature there is a drastic deterioration of the mechanical properties of the polymer. The crystalline isotactic poly(styrene) has not found any industrial use because of its low crystallization rate. However, crystalline syndiotactic poly(styrene) shows a high melting point, about 270°C, and a relatively

Table A.1 Polystyrene Properties

Property	Atactic polystyrene	Isotactic polystyrene	Syndiotactic polystyrene
Solubility	Acetone/MEK	Insoluble in acetone/MEK	Insoluble in acetone/MEK
Tg,°C	100	100	100
Tm,°C	-	225 to 240	265 to 270
Crystallinity	Amorphous	Crystalline	Crystalline
Rate of crystallization.	-	slow crystallization rate	fast crystallization rate
IR, cm^{-1}	-	1364, 1314, 1297, 1185	1200-1220
^{1}H NMR			
Methine proton,ppm	2.05 (singlet) broad	2.3 (triplet)	1.9 (triplet)
Methylene protons,ppm	1.6 (singlet) broad	1.7(octet) (non equivalent)	1.45 (triplet) (equivalent)
^{13}C NMR			
Carbon 1, ppm (substituted phenyl carbon)	145.12-146.77 (pentet)	146.24 (singlet)	145.13 (singlet)

high crystallization rate. The thermal and structural characteristics of syndiotactic polymer allow retention of its mechanical properties even at temperatures higher than the Tg.

Dow Chemical, USA and Idemitsu Petrochemical , Japan have started production of syndiotactic poly(styrene) using single site metallocene compounds in a pilot plant (27 tonne/year), located at Chiba, Japan[7]. The major target applications for syndiotactic poly(styrene) is primarily as an engineering resin for both injection molding and extrusion applications as well as constituent in blends.

Synthesis and characterization of syndiotactic poly(styrene)

Syndiospecific polymerization of styrene can be promoted by homogeneous catalytic systems consisting of methylaluminoxane and soluble compounds of titanium or zirconium such as tetrabenzyltitanium, tetrabenzylzirconium, (cyclopentadienyl) titaniumtrichloride, titanium or zirconium alkoxides[6,8,9]. Among them, titanium alkoxides, in particular titanium-n-butoxide (TNB), in conjunction with methylaluminoxane has been studied extensively as a syndiospecific polymerization catalyst. The titanium alkoxide based catalyst systems, in general, have shown low activity (20 - 50 kg. of polymer/mol Ti/mol styrene/h) and poor conversion (2-4)%[9]. It has been recently reported that supported catalysts, $SiO_2/Ti(OBu)_4$, $MgCl_2/Ti(OEt)_4$ in conjunction with methylaluminoxane produce syndiotactic poly(styrene)[10,11]. High catalyst activity with high degree of syndiospecificity was achieved by using homogeneous monocyclopentadienyl titanium tributoxide with methylaluminoxane[12]. The organometallic compounds Cp^*TiBz_3, $Cp^*Ti(CH_3)_3$ (Cp^* = neopentamethyl cyclopentadienyl) were lately reported by Pellechia *et al.* for the preparation of poly(styrene) in conjunction with $B(C_6F_5)_3$[13]. The available data in the literature on the synthesis of syndiotactic poly(styrene) using different catalysts are shown in Table A.2.

Different analytical techniques such as ^{13}C-NMR, ^1H-NMR, FT-IR, DSC, X-ray analysis and insolubility in acetone or methylethyl ketone have been employed to measure the degree of syndiotacticity of poly(styrene). ^{13}C-NMR spectrum of syndiotactic poly(styrene) shows a characteristic chemical shift at 145.3 ppm in comparison to a sharp peak at lower field at 146.24 ppm in the case of isotactic

Table A.2 Syndiospecific Polymerization of Styrene-Literature Data

Catalyst	Temp. (°C)	Time (h)	Convn. (%)	Activity x 10^{-3} (gPS/mol.Ti/mol.M/h)	Syndiotacticity (%)	$\bar{M}w$	$\bar{M}n$	$\bar{M}w/\bar{M}n$	Ref.
$CpTiCl_3$-MAO	50	2	99.2	66.9	syndiotactic	-	-	-	6c
$Ti(OBu)_4$-MAO	60	1.7	1.6	53.8	86	361000	98000	3.7	22
$CpTiCl_3$-MAO	50	1.7	5.4	133.8	91	96000	34300	2.8	21
$Ti(Bz)_4$-MAO	60	1	6.8	139.0	87	96900	19000	5.1	20
$CpTi(OBu)_3$-MAO	50	0.5	77.0	29600.0	80	38000	8600	4.4	12
$Ti(OEt)_4$-MAO	50	4	3.4	20.2	96	442000	149000	3.0	11
$Ti(OEt)_3Cl$-MAO	50	4	2.3	4.0	97	175000	48000	3.6	11
$MgCl_2/Ti(OEt)_4$-MAO	50	4	1.5	88.6	98	330000	84600	3.9	11
$SiO_2/Ti(OBu)_4$-MAO	40	3	19.8	6.9	100	330000	194100	1.7	9
$Cp^{*}TiBz_3$-$B(C_6F_5)_3$	50	0.17	66.0	2.5	high syndiotacticity	-	-	-	13

poly(styrene)[14]. Similarly DSC shows a Tm of 260-270^{0}C for syndiotactic poly(styrene)[14]. FT-IR spectrum also shows a marked difference between syndio and isotactic poly(styrene)[11]. Amorphous poly(styrene) (richer in atactic content, as evidenced by the presence of considerable % of mr triads) is soluble in boiling acetone and boiling methylethyl ketone whereas, crystalline poly(styrene) (both isotactic and syndiotactic, indicated by the presence of considerable % of mm and rr triads respecitvely and absence of significant % of mr triads) is insoluble both in boiling acetone and boiling methylethyl ketone. Zambelli[8,14] has used boiling acetone for determining the insoluble syndiotactic poly(styrene) content in poly(styrene) whereas, other workers have employed boiling methylethyl ketone[9,10,12].

In general, methylaluminoxane is the preferred cocatalyst component for syndiotactic polymerization of styrene. Sterically crowded organoaluminum compounds have attracted attention recently as components of Ziegler-Natta catalysts for the polymerization of α-olefins[15,16]. As cocatalyst components in heterogeneous Ziegler-Natta catalysts they have been found to improve both stereoselectivity and activity. However, such sterically crowded organoaluminum compounds have not been reported as components of homogeneous catalysts for the polymerization of styrene.

We therefore undertook a brief study of styrene polymerization using titanium-n-butoxide and a sterically crowded organoaluminum compound derived from the reaction of trimethylaluminum with butylated hydroxy toluene.

A.2 Experimental Section

All operations were carried out under dry nitrogen using standard bench top inert atmosphere techniques.

A.2.1 Materials

Methylaluminoxane (Schering, A.-G., Germany) was used as received (5.8% Al, average molecular weight = 850, methane/aluminum = 1.22). Double distilled styrene was stirred over calcium hydride for 24 h in inert atmosphere. This was distilled under reduced pressure over CaH_2 before use. Titanium-n-butoxide (TNB) was vacuum distilled twice and was further purified by adding triisobutylaluminum (2 mL in 10 mL of hexane) to 15 mL of TNB dropwise at room temperature. The color of the solution turned black. The mixture was stirred for half an hour and distilled at 120 °C/0.5 mm of Hg. The distilled product is used as TNB catalyst for the polymerization. AlMe(BHT)$_2$ was prepared and characterized as reported in chapter 2. Toluene (Loba-AR Grade, Bombay) was refluxed over sodium wire for 48 hours and finally distilled out just prior to use.

A.2.2 Polymerization

All polymerizations were performed in 25 mL capacity single necked round bottomed flask equipped with a septum inlet. The polymerization temperature was maintained by using constant temperature water bath. A typical procedure is as follows.

Freshly distilled styrene (5mL) was placed in a r.b. flask. Subsequently, the required amount of toluene solution of AlMe(BHT)$_2$ was added to the flask. The polymerization was initiated by introducing the required amount of toluene solution of titanium-n-butoxide. The reaction mixture was heated in a constant temperature bath for the desired temperature and time. The polymerization was terminated by addition of 10% acidified methanol. The polymer was washed with excess methanol and dried in vacuo for 4 h at 50^{0}C. The poly(styrene) was characterized by ^{13}C-NMR, DSC, solubility in boiling acetone and intrinsic viscosity measurements.

A.2.3 Analysis

^{13}C-NMR spectra of the acetone insoluble poly(styrene) was obtained in o-dichlorobenzene as well as in CDCl$_3$ on an MSL-300 Bruker NMR spectrometer at ambient temperature. Thermal analysis of the polymer were carried out using Perkin Elmer DSC-7 instrument. Intrinsic viscosity of the poly(styrene) was determined in tetrahydrofuran at 30°C at a concentration of 0.5 g/dL.

A.3 Results and discussion

Styrene was polymerized in toluene at various Al/Ti molar ratio in the temperature range of 50-90^{0}C and reaction time varying between 5 and 10 hours. The results are given in Table 2. The polymer was soxhlet extracted using acetone for 4 hours and the fraction insoluble in boiling acetone was determined.

Poly(styrene) obtained using the TNB-AlMe(BHT)$_2$ was found to be insoluble in boiling acetone (80-95% acetone insoluble). Both yield and % of acetone insoluble fraction increase with increase in polymerization temperature. However, molecular weight decreases with increasing temperature (Table A.3). Similarly yield and acetone insoluble fraction content increase with increasing reaction time. The polymer yield is almost invariant with Al/Ti molar ratio in the range of 25-200. However, upon increasing the concentration of AlMe(BHT)$_2$, both the % of acetone insoluble fraction and molecular weight decrease. Titanium phenoxide and zirconocene were also found to polymerize styrene; however, with zirconium catalyst the % of acetone insoluble fraction was low. Koida *et al.* [17]., polymerized styrene using TNB in presence of triethylaluminum and observed that the activity was at its maximum at an Al/Ti ratio of 1.5. At Al/Ti ratio of 1.5 the conversion was found to be 20%. When the ratio exceeded 3, the activity became negligible. However, when the organoaluminum compound is replaced with AlMe(BHT)$_2$ and is used along with TNB, a much higher Al/Ti ratio of 25-200 is required and shows practically no change in the activity with varying Al/Ti ratios.

Poly(styrene) (acetone insoluble fraction) obtained from the above reactions was characterized by ^{13}C-NMR spectroscopy and DSC. Phenyl C-1 carbon of poly(styrene) appeared as a group of signals in the range of 144-146.5 ppm indicating the atactic nature of the poly(styrene) (Figure A.1). Further, signals appearing in the range of 41.5 to 47 ppm are reflective of stereochemical configurations. Assignments of chemical shifts due to various tetrad sequences are available in the literature[4]. From the intensities of these signals, triad concentrations were calculated employing the triad-tetrad relationships[18,19]. (Equations A.1, A.2 and A.3)

Table A.3 Polymerization of Styrene[a]

Entry No.	catalyst	cocatalyst	Al/Metal (mol ratio)	Temperature (^0C)	Time (h)	Conversion (%)	Residue of acetone extraction (%)	$[\eta]^b$ (dL/g)
1	$Ti(OBu)_4$	$AlMe(BHT)_2$	27	70	5	4.6	89	0.75
2	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	70	5	4.5	87	0.68
3	$Ti(OBu)_4$	$AlMe(BHT)_2$	110	70	5	4.2	85	0.39
4	$Ti(OBu)_4$	$AlMe(BHT)_2$	200	70	5	4.9	83	0.36
5	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	50	5	1.5	86	0.58
6	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	60	5	1.8	90	0.58
7	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	90	5	10.5	90	0.50
8	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	70	3	2.8	88	0.39
9	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	70	4	3.1	89	0.39
10	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	70	7	5.4	95	0.51
11	$Ti(OBu)_4$	$AlMe(BHT)_2$	55	70	10	9.8	90	0.53
12	$Ti(OPh)_4$	$AlMe(BHT)_2$	50	70	5	3.5	91	0.74
13	Cp_2ZrCl_2	$AlMe(BHT)_2$	50	70	5	2.6	58	0.54
14	$Ti(OBu)_4$	MAO	55	70	5	7.7	93	0.72

[a] Polymerization conditions: styrene = 5mL, Toluene = 5mL, $Ti(OBu)_4 = 2.56 \times 10^{-2}$ mmol, $Ti(OPh)_4 = 3.035 \times 10^{-2}$ mmol, $Cp_2ZrCl_2 = 3.0477 \times 10^{-2}$ mmol.

[b] Intrinsic viscosity was determined in THF at 30^0C at a concentration of 0.5 g/dL.

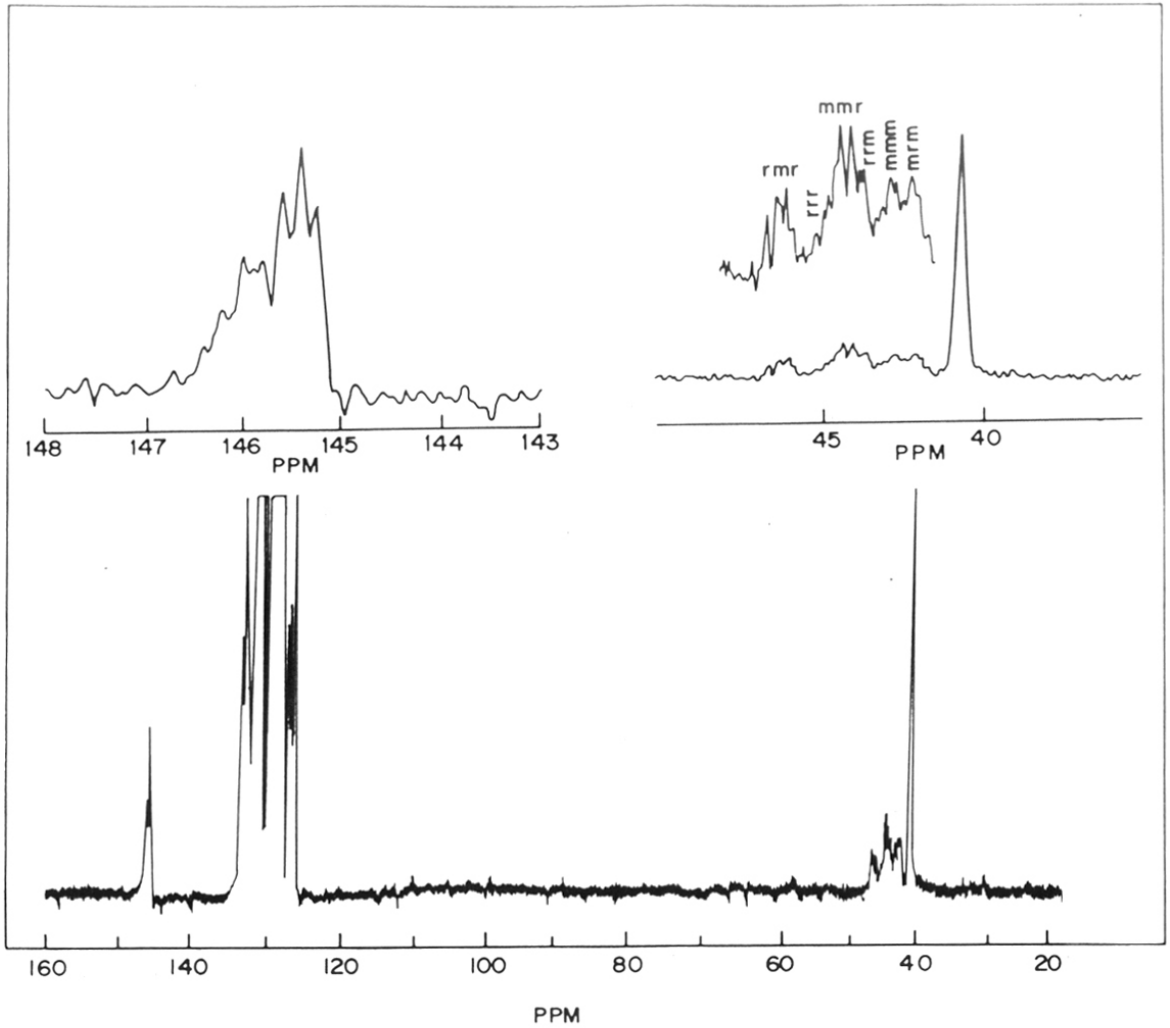

Fig. A.1 75.5 MHz ^{13}C-NMR spectrum of acetone insoluble fraction of poly(styrene) prepared by using TNB-AlMe(BHT)$_2$ catalyst in ODCB at 30°C mm = (mmm) + 1/2 (mmr) (A.1)

mr = mrr + 2(mrm) (A.2)

rr = rrr + 1/2 (mrr) (A.3)

Tetrad concentrations derived from ^{13}C-NMR

(mmm) = 19.287, (mmr+rmm) = 32.359, (rmr) = 17.390,
(mrm) = 20.133, (mrr+rrm) = 14.222, (rrr) = 7.814

Triad (mm, mr and rr) concentrations were calculated by substituting the tetrad concentrations in the equations A.1, A.2 and A.3.

mm = 19.287 + 1/2(32.359) = 35.465
mr = 14.222 + 2(20.133) = 54.488
rr = 7.814 + 7.111 = 14.925

$$\% \text{ mm} = \frac{\text{mm}}{\text{mm} + \text{mr} + \text{rr}} \times 100 = 33.8$$

$$\% \text{ mr} = \frac{\text{mr}}{\text{mm} + \text{mr} + \text{rr}} \times 100 = 51.9$$

$$\% \text{ rr} = \frac{\text{rr}}{\text{mm} + \text{mr} + \text{rr}} \times 100 = 14.2$$

Thus mm, mr and rr triad concentrations were observed to be 33.8, 51.9 and 14.2% respectively. This indicates that the polymer produced by this catalyst is predominantly atactic in nature. This is confirmed by DSC which showed a Tg at 100^{0}C (Figure A.2). The polymer was found to be practically insoluble in boiling acetone; but completely soluble in methylethylketone. Thus, one can conclude that insolubility in boiling acetone is a necessary but not sufficient condition of tacticity. In contrast, the acetone insoluble fraction of poly(styrene) synthesized using

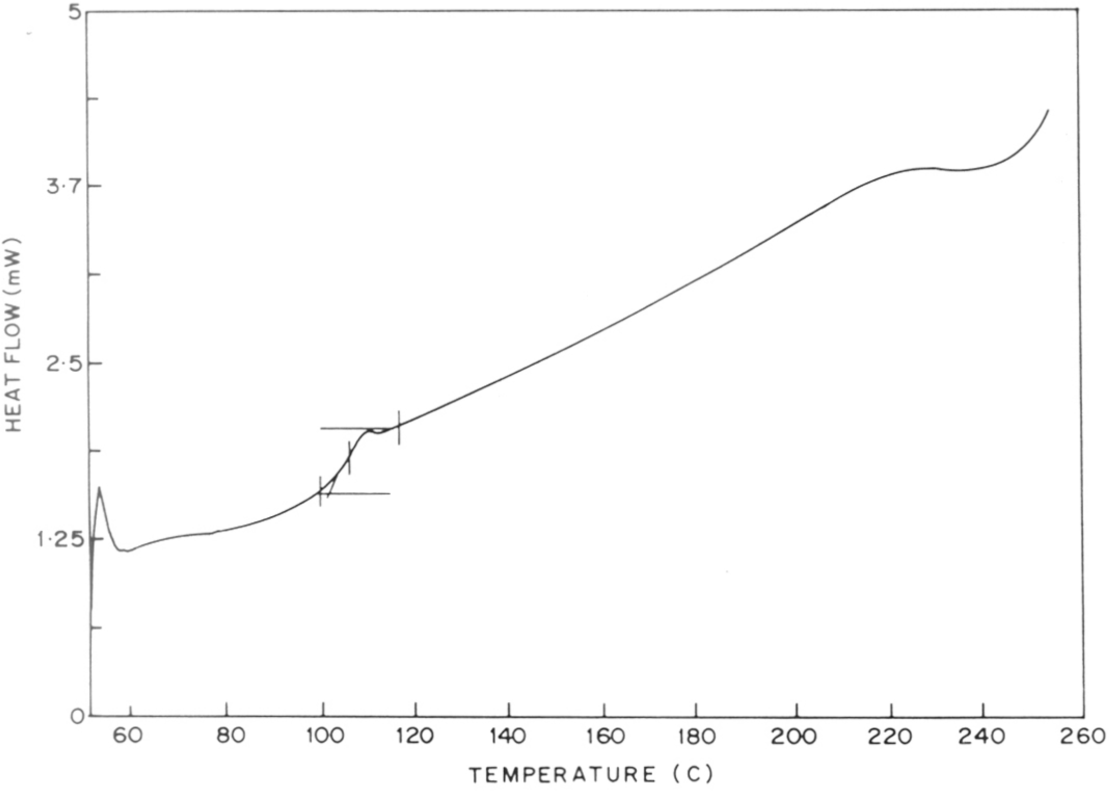

Fig. A.2 DSC endotherm of poly(styrene)

$Ti(OBu)_4$-MAO catalyst system (Entry No. 14 of Table A.3) showed a single peak (Figure A.3) at 145.3 ppm indicating the syndiotactic nature of the polymer. This polymer was insoluble in both boiling acetone and in methylethyl ketone.

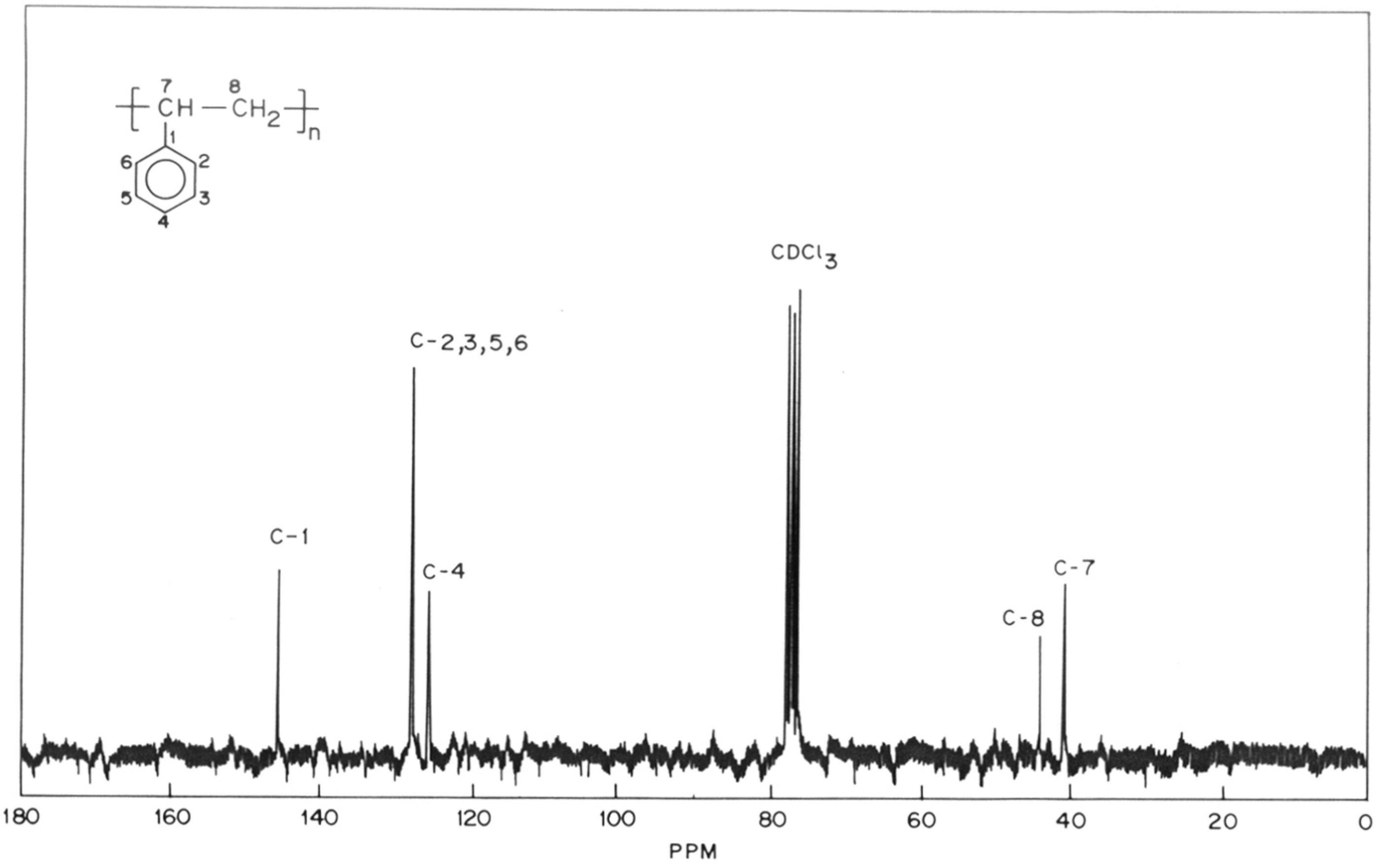

Fig. A.3 75.5 MHz ^{13}C-NMR spectrum of acetone insoluble fraction of poly(styrene) prepared by using TNB-MAO catalyst in $CDCl_3$ at 30°C

A.4 References

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SYNOPSIS

The thesis entitled "**A Study of Methylaluminoxane Catalyzed Homogeneous Ziegler-Natta Polymerization of Ethylene and Photopolymerization of Acrylic Monomers**" is divided into two parts - Part A deals with polymerization of ethylene using bis(cyclopentadienyl)zirconiumdichloride-methylaluminoxane catalyst systems and is subdivided into four chapters. Part B which deals with methylaluminoxane induced photopolymerization of acrylic monomers is further divided into two chapters. Chapter VII summarizes the work reported in the thesis.

PART - A

Introduction

Ever since the discovery of homogeneous bis(cyclopentadienyl)titanium(IV) dichloride (Cp_2TiCl_2)-alkylaluminum catalyst system for ethylene polymerization, homogeneous Ziegler-Natta catalysts have assumed importance for a variety of fundamental and applied reasons[1]. Recent discoveries in the area of homogeneous, highly active and stereospecific metallocene-aluminoxane catalysts[2] has stimulated renewed commercial and academic interest in these catalysts[3]. This is evidenced by the accumulation of large volume of patented and published literature during the last 15 years.

Any hydrocarbyl aluminum compound on controlled reaction with water forms an aluminoxane. The most commonly used alkylaluminums for the synthesis of aluminoxanes are trimethylaluminum (TMA), triethylaluminum (TEAL) and triisobutylaluminum (TIBAL). Of the various aluminoxanes, methylaluminoxane (MAO) is the most difficult to prepare because of the extreme reactivity of TMA. However, the most reactive MAO is the most preferred one for olefin polymerization.

Metallocene-MAO based catalysts are well studied homogeneous Ziegler-Natta catalysts for olefin polymerization. The present investigation was undertaken with a view to understand some of the features of MAO based homogeneous Ziegler-Natta catalysis as described below.

a) The reaction between water and alkylaluminums is highly exothermic, accompanied by flames and yields aluminum oxide. MAO, whose structure has been postulated as a mixture of linear and cyclic oligomers of $[Al(Me)O]_n$ units, is prepared by controlled, partial hydrolysis of TMA with hydrated salts in an inert solvent medium, preferably toluene[4]. Recently, on the basis of X-ray structural characterization, Barron et.al., have proposed that MAO and related aluminoxanes have cluster structures analogous to those found for the iminoalanes in which the aluminum centers are tetra-coordinate[5]. Depending on the nature of salt used and the reaction conditions, MAO with widely differing activities as co-catalysts in polymerization of ethylene is formed[4]. It is reported that MAO forms an adduct with three molecules of TMA which even after distillation in the presence of cumene or complexation with tetrahydrofuran retains one molecule of strongly associated TMA[6]. The structure, degree of oligomerization, methane/aluminum molar ratio, and the amount of free or complexed TMA to MAO will differ depending on the reaction conditions like nature of water source, temperature, water to alkylaluminum ratio, and concentration of alkylaluminum during synthesis employed for the preparation of MAO.

Despite of large volume of published and patented literature on MAO, details of its structure, degree of oligomerization, methane/aluminum molar ratio, the amount of free or complexed TMA to MAO are not well understood. The effect of free TMA on polymerization of ethylene using metallocene-MAO catalyst system has not been well studied so far.

b) Sterically hindered aryloxy derivatives of alkylaluminums have been shown to polymerize propylene and isoprene using $TiCl_3$ catalyst[7]. TMA on reaction with sterically hindered phenol like butylated hydroxy toluene gives a compound $AlMe(BHT)_2$, which is monomeric in nature and bears a close similarity to the structure of oligomeric MAO[8]. The $AlMe(BHT)_2$ which has been reported to act as a cocatalyst in heterogeneous Ziegler-Natta catalysis has not been used as a catalyst component along with metallocenes for the polymerization of ethylene so far.

Objective of present investigation

1. To synthesize MAO at different reaction conditions, characterize the synthesized MAO for methane/aluminum molar ratio, molecular weight and % of TMA, and to study the catalytic effect of the synthesized MAO on ethylene polymerization using Cp_2ZrCl_2 catalyst.
2. To study the effect of added TMA to MAO, and to study the various reaction conditions like temperature, Al/Zr ratio, concentration of Cp_2ZrCl_2 and concentration of MAO on polymerization of ethylene using Cp_2ZrCl_2 catalyst. Also the effect of $AlMe(BHT)_2$ as a cocatalyst on polymerization of ethylene using Cp_2ZrCl_2 as catalyst also is to be investigated.

Chapter - I

This chapter provides a historical background of the Ziegler-Natta catalyst systems, a detailed literature survey of aluminoxanes (mainly MAO) synthesis, characterization and a critical survey of homogeneous Ziegler-Natta catalysts for the polymerization of ethylene.

Chapter - II

The objective and scope of the present investigation is described in this chapter.

Chapter - III

This chapter deals with the synthesis of MAO using hydrated salts at different reaction conditions as shown in the equation.

$$Al(CH_3)_3 \xrightarrow[\text{partial hydrolysis}]{\text{hydrated salt, toluene}} [-Al(CH_3)-O-]_n$$

Methyl/aluminum ratio obtained for MAOs synthesized by different methods are compared. The percentage of hydrolysis with time for MAOs synthesized by different methods are discussed. MAO obtained has been characterized by ^1H-NMR, cryoscopy and analytical techniques. The molecular weights determined by cryoscopy and methane/aluminum molar ratio determined by ^1H-NMR and analytical techniques are compared for different MAOs. MAOs prepared by different reaction conditions are also compared for their catalytic activity on ethylene polymerization using Cp_2ZrCl_2 catalyst at one atmosphere pressure and using toluene as solvent.

Chapter - IV

This chapter deals with the polymerization of ethylene in toluene at one atmosphere pressure using bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) catalyst and MAO, TMA, tetraisobutyldialuminoxane (TIBDAO) (Schering-A.G., Germany) and sterically hindered aryloxy derivative of TMA, $AlMe(BHT)_2$ (synthesized in the laboratory) as cocatalysts.

The role of TMA on Cp_2ZrCl_2-MAO catalyzed polymerization kinetics of ethylene has been studied. By the addition of TMA to the Cp_2ZrCl_2-MAO system for the polymerization of ethylene the kinetic profile changes from a decay type curve to a build up type curve. Increase in catalytic activity as well as life time of the catalyst are also observed.

The effect of concentration of different cocatalysts mentioned above, effect of [Zr] and temperature on kinetics of ethylene polymerization are also discussed in this chapter. Higher activity and higher rate of polymerization are observed at high Al/Zr ratio, higher temperature (70°C) and lower [Zr]. $AlMe(BHT)_2$ does not polymerize ethylene in conjunction with Cp_2ZrCl_2. However, the addition of TMA to the Cp_2ZrCl_2-$AlMe(BHT)_2$ system makes it an active catalyst for polymerization of ethylene. The kinetic profile changed from build up type to decay type curve which is reminiscent of MAO cocatalyzed ethylene polymerization.

The synthesized polyethylenes have been characterized by DSC, TGA and intrinsic viscosity measurements.

PART - B

Introduction

Among the various polymerization methods for vinyl and related monomers radical polymerization has been known for the longest time and is best understood. This method requires the introduction of a radical species into the monomeric system. The most common way of generating radicals is by homolytic decomposition of covalent bonds. This can be achieved by imparting enough energy to the bond, either by heating or by radiation. Photochemical reactions, either catalyzed or uncatalyzed, can also lead to initiation of free radical polymerization of vinyl and related monomers.

Photopolymerization of methyl methacrylate induced by triethylaluminum has been reported to proceed via free-radical mechanism[9]. A photoexcited state of the carbonyl complex of the Wittig "ate" type has been proposed as the active initiator. Recently, Inoue and co-workers have studied the light-induced polymerization of methyl methacrylate using aluminum tetraphenylporphyrin as initiator[10]. The reaction has been shown to proceed by a concerted mechanism involving the enol ester of methyl methacrylate bound to aluminum as the active species. The polymerization exhibits the characteristics of a living polymerization such as controlled and predictable molecular weight and narrow molecular weight distribution.

Photopolymerization of methyl methacrylate and other acrylic esters induced by MAO has not been studied so far.

Objective of the present investigation

To study the polymerization of acrylic monomers induced by MAO and TMA in presence of U.V. light.

Chapter - V

This chapter provides a brief introduction to the photopolymerization, principles of photopolymerization and kinetic features of photopolymerization of acrylic ester monomers. Objective of the present investigation is also discussed.

Chapter-VI

The features of polymerization of acrylic ester monomers induced by TMA and MAO in U.V. light are compared in this chapter. The effect of time and conversion on number average molecular weight for TMA as well as MAO initiated photopolymerization of methyl methacrylate have been studied. With MAO, both conversion and number average molecular weight increase linearly with time. The plot of number average molecular weight versus conversion is also linear. This behavior is reminiscent of the "living" radical polymerization of methyl methacrylate observed with thermal iniferters and photoiniferters. The molecular weights of poly(methyl methacrylate)s achieved in the case of MAO-induced photopolymerization of methyl methacrylate are much higher than those obtained through TMA-induced photopolymerization. The features of MAO-induced photopolymerization of methyl methacrylate differ significantly from that of pure TMA. The kinetics of photopolymerization of methyl methacrylate induced by MAO and TMA have also been studied.

The synthesized polymers have been characterized by ^{1}H-NMR, TGA, DSC, GPC and intrinsic viscosity measurements.

Chapter - VII

This chapter summarizes the results and describes the salient conclusions of the investigations reported in the thesis.

PART - A

The study has resulted in a better understanding of the different synthetic routes for the preparation of MAO and the effect of synthesis conditions on the catalytic effect of MAO for the polymerization of ethylene. Synthesized MAO has been thoroughly characterized. The Cp_2ZrCl_2-TIBDAO catalyst system has been shown to polymerize ethylene with a kinetic profile similar to that of Cp_2ZrCl_2-MAO catalyzed polymerization of ethylene with a low activity. The studies on the effect of added TMA on Cp_2ZrCl_2-MAO catalyzed polymerization of ethylene resulted in increase in the catalytic activity as well as increase in life time of the catalyst accompanied by a change in kinetic profile from decay type to build up type curve.

The Cp_2ZrCl_2-$AlMe(BHT)_2$ catalyst system has been shown to polymerize ethylene in presence of added TMA with a kinetic profile similar to that of Cp_2ZrCl_2-MAO catalyzed polymerization of ethylene with a low activity. These results have been explained based on the current understanding of the mechanism of ethylene polymerization using homogeneous metallocene-MAO catalyst.

PART - B

The photopolymerization studies resulted in the use of MAO as a photoinitiator for the polymerization of acrylic ester monomers. MAO induced polymerization showed a linear increase in conversion as well as number average molecular weight with time. A linear increase in number average molecular weight with conversion for the photopolymerization of methyl methacrylate is also observed. The kinetic parameter k_p^2/k_t for the photopolymerization of methyl methacrylate induced by MAO is found to be 20 times higher than that of TMA.

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LIST OF PUBLICATIONS / PATENTS

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2. S. Srinivasa Reddy, G. Shashidhar and S. Sivaram
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