Propylene Polymerization Using MgCl$_2$/Ethylbenzoate/TiCl$_4$ Catalyst: Determination of Titanium Oxidation States

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ABSTRACT: The chemical interaction of the catalyst MgCl$_2$/ethylbenzoate/TiCl$_4$ with the cocatalysts triethylaluminum and trisobutylaluminum was investigated to establish a relationship between the titanium oxidation states and the catalytic activity, polymer isotacticity, and polymer molecular weight in propylene polymerizations. This interaction was studied using different Al : Ti molar ratios by measuring the changes of the titanium oxidation states at different polymerization times. Both hydrogen and alkyl aluminum caused a reduction of Ti^{4+} species to lower oxidation states species Ti^{3+} and Ti^{2+}. However, the Ti^{4+} species reduction appeared to be incomplete. It was found that the Ti^{4+} species undergoes a severe reduction as the Al : Ti molar ratio increases from 50 to 230 as overreduction takes place. This change of the Ti^{3+} species percentage with time was found to correlate with the rate–time profiles of propylene polymerization. From this observation, it would be fair to conclude that the trivalent titanium species is more likely to be the active titanium species for propylene polymerization than the aforementioned catalyst system. On the other hand, hydrogen addition was found to cause an increase in Ti^{3+} species. The increases in both hydrogen amount and/or Al : Ti molar ratio were found to cause a decrease in both molecular weight and polypropylene isotactic index. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 56–62, 2004

Key words: Ziegler–Natta polymerization; supports; propylene polymerization; titanium oxidation states; isotactic

INTRODUCTION

Since the discovery of Ziegler–Natta catalysts, there has been little mention in the literature of determinations of the oxidation states of the transition metal ions and their behavior during the polymerization reaction. For instance, both TiCl$_4$–AlEt$_3$ and TiCl$_4$–AlEt$_2$Cl catalyst systems that were originally used are known to contain various amounts of three different titanium valences, Ti^{4+}, Ti^{3+}, and Ti^{2+}.

The emergence of the stereospecific catalyst δ-TiCl$_3$·0.33AlCl$_3$–AlEt$_2$Cl, which was used for propylene polymerization, displaced the original catalyst systems and interest concerning their active valence states waned.

The interest in the titanium valence states was renewed[1–4] when high-activity catalysts, supported on magnesium chloride, were formulated.[5] The main reason behind that was the fact that a significant fraction of the titanium ions in these catalyst systems were catalytically active. Also these catalysts are kinetically characterized by a very rapid decay in activity. Thus the determination of both titanium species oxidation states and active site concentration may help to identify the valences of titanium species that are active for the polymerization. Depending on whether there is a parallel change in the distribution of titanium oxidation states, one may gain an understanding about the mechanism of the catalyst deactivation.[6] The literature shows different procedures and methods to determine the concentrations of Ti^{2+}, Ti^{3+}, and Ti^{4+}. Redox titration was used by Goto and Takeyama[7] to determine [Ti^{2+}], [Ti^{3+}], and [Ti^{4+}]. Kashiwa et al.[2] used H$_2$ evolution for [Ti^{2+}] determination and polarography for determination of [Ti^{3+}] and [Ti^{4+}]. Baulin et al.[8] used potentiometric titrations for [Ti^{n+}] determination. Chien et al.[6] used two redox titrations for ([Ti^{3+}] + [Ti^{2+}]) and ([Ti^{3+}] + 2[Ti^{2+}]) determination and atomic adsorption for [Ti^{n+}] determination, whereas [Ti^{4+}] was obtained by working out the difference.

EXPERIMENTAL

Reagents

Polymerization-grade propylene, nitrogen (99.99% pure), and hydrogen (99.99% pure) were supplied by the British Oxygen Company Ltd. (London, UK). Gases were purified using columns of preactivated molecular sieves (types 4A and 13X).

n-Heptane (99+% pure), *n*-hexane (99+% pure), and anhydrous isopentane (99+% pure) were ob-

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tained from Sigma–Aldrich Chemical Co. Ltd. (Shaftesbury, UK). Solvents were stored for 24 h over activated molecular sieves (types 13X and 4A), then purged with dried nitrogen before use.

Triethyl aluminum and triisobutyl aluminum, as 1.0M solutions in hexane, and neat titanium tetrachloride (99.9% pure) were obtained from Sigma–Aldrich.

Ethylbenzoate (EB), obtained from BDH Chemicals Ltd. (Poole, UK), was dried over calcium hydride for 24 h before being vacuum distilled and stored over activated molecular sieves (type 4A) in an inert atmosphere of dry nitrogen.

Ammonium ferric sulfate dodecahydrate, potassium thiocyanate, and potassium diphenylamine sulfonate were obtained from Jansen Chimica (Geel, Belgium).

Two types of molecular sieves, 13X and 4A, anhydrous magnesium chloride, and GPR-grade decalin 97% were obtained from BDH Chemicals Ltd.

Catalyst preparation

The catalyst was prepared according to a modified preparation procedure as described in the patent literature as follows:[9,10]

Anhydrous magnesium chloride (102 g, 1.07 mol) was vacuum dried for at least 8 h at 150°C. This was mixed with 3.89 cm^3 of SOCl$_2$ (MgCl$_2$: SOCl$_2$ molar ratio = 20 : 1) and then ball-milled for 1 h at room temperature to achieve further chemical drying. EB (31.25 cm^3), giving a MgCl$_2$: EB ratio of 7.5 : 1, was added and the mixture was then further ball-milled for another 70 h. The final ball-milled product was transferred under nitrogen to a flask and stored in a dry box.

A 10-g sample of the ball-milled product was transferred under nitrogen into the catalyst preparation vessel (CPV). The CPV was placed in an oil bath, and its contents were stirred and treated with 40 cm^3 of TiCl$_4$ at 80°C for 2 h to form a slurry. This slurry was filtered at 80°C and then washed with three portions of n-heptane 20 cm^3 forming a solid phase. This product was then treated with 40 cm^3 of CCl$_4$ at 70°C for 1 h, filtered, and treated with 40 cm^3 of TiCl$_4$ at 80°C for 1 h more. This slurry was filtered at 80°C and then washed with several 20 cm^3 portions of n-heptane until the filtrate was free of Ti compounds.

The solid product (catalyst) was dried under vacuum at 70°C for 24 h and stored in a dry box. Some of the dried catalyst powder was made into a final slurry form by addition to n-hexane. The Ti concentration of the slurry was determined as being 0.01M by a colorimetric method.

Polymerization procedure

Polymerization reactions were performed in a slurry phase using a high-pressure jacketed reactor system of 500 cm^3 capacity (Ecoclave 150; Büchi AG, Uster, Switzerland). Polymerizations were performed under the following conditions of [Ti] = 0.05 mmol dm^{-3}, 60°C, 2 h, 250 cm^3 of hexane as solvent, 300 rpm agitation speed using an anchor-type stirrer, and 1 bar as a total pressure of propylene and hydrogen. The propylene pressure was maintained and monitored, and its consumption accurately measured using a mass flow meter.

The adopted polymerization procedure was essentially that used by previous workers.[11,12] The first stage of the procedure involved purification of the reactor by backing the reactor under vacuum at 95°C for 1 h. Reactor temperature was cooled to 60°C and then propylene was admitted to the reactor up to a pressure of 1 bar. The solvent, n-hexane (250 cm^3), was charged to the reactor vessel through a suba-seal injection port using a needle canula. The required amounts of starting materials (hydrogen, cocatalyst, and catalyst) were all sampled through a suba-seal injection port using gas-tight luer-lock syringes and needles (18–14 gauge). Before use the syringes and needles were thoroughly washed with soap, water, and acetone and dried in an oven at 160°C. The needles were cooled and primed with n-hexane solvent to exclude air bubbles and the required materials (cocatalyst and catalyst) were sampled under a continuous stream of dry nitrogen.

The materials were introduced sequentially, with about 4 min between each addition, and the following order was used: hydrogen, cocatalyst, and finally catalyst slurry. After 2 h of polymerization, the reaction was terminated by closing off the gaseous monomer supply and evacuating any remaining gas. The reactor contents were removed through the reactor outlet at the base of the vessel while the reactor vessel was being purged with dry, oxygen-free nitrogen gas. A small quantity of propan-2-ol (25 cm^3) was added to the resulting mixture to help precipitate low molecular weight polymers and to remove any catalyst or cocatalyst residues that might have been present. The resulting polymer was allowed to settle, then filtered, and finally dried in an oven at 60°C. The weight of the polymer produced was determined by an analytical balance.

Average molecular weight determination

The intrinsic viscosity of each copolymer solution in decalin at 134 ± 1°C was measured using a Ubbelohde suspended level viscometer (Cannon–Ubbelohde, State College, PA). Once the intrinsic viscosities had been measured it was possible to calculate the viscosity-average molecular weights for the polymers using the following equation[11]: $[\eta] = 11.0 \times 10^{-5} \times (\overline{M}_v)^{0.80}$.

Polymer isotacticity determination

Polypropylene isotacticity was determined by using the procedure developed by Natta et al.[13] A 1-g sample of polypropylene was extracted with boiling *n*-heptane solvent for 24 h using Soxhlet extraction. The weight percentage of *n*-heptane (insoluble) was taken as the isotactic index (I.I.).

Determination of titanium oxidation states

Redox titrations

The oxidation states of Ti were determined by redox titrations using the methods of both Goto and Takeyama[7] and Chien et al.[6] In the present study titration (A) of Goto and Takeyama's method was used to determine the value of $[Ti^{3+}] + 2[Ti^{2+}]$, and titration (B) of Chien's method was used to determine the value of $[Ti^{3+}] + [Ti^{2+}]$.

Because the polymerization slurry samples were air sensitive, a sealed system was used, consisting of an Erlenmeyer flask connected to a burette by a connection equipped with tap, suba-seals, and inert gas inlet and outlet. All solvents, solutions, and chemicals were flushed with dry oxygen-free nitrogen before each titration.

Method of Goto and Takeyama: titration (A) (hydrolysis method)

A 10-cm^3 sample from the polymerization slurry, containing about 7×10^{-5} g of titanium, was withdrawn from the reactor at different time intervals through a suba-seal injection port using gas-tight luer-lock syringes and needles. The sample was injected into a 200-cm^3 Erlenmeyer flask of the sealed system, containing 50 cm^3 of oxygen-free water and 8 cm^3 sulfuric acid. A 40 wt % KSCN solution (2.5 cm^3) was injected and used as an indicator. A burette containing 0.005M ammonium ferric sulfate solution was used for the titration in this procedure under CO$_2$ atmosphere.

From this titration it was possible to calculate $[Ti^{3+}] + 2[Ti^{2+}]$.

Method of Chien: titration (B)

A 10-cm^3 sample from the polymerization slurry, containing about 7×10^{-5} g of titanium, was withdrawn from the reactor at different time intervals through a suba-seal injection port using gas-tight luer-lock syringes and needles. The sample was injected into a 200-cm^3 Erlenmeyer flask of the sealed system, containing 20 cm^3 of oxygen-free water and 2 cm^3 of concentrated sulfuric acid. Potassium diphenylamine sulfonate (1 g in 50 cm^3 H$_2$O) was injected and used as an indicator. A burette containing 0.005M potassium dichromate (K$_2$Cr$_2$O$_7$) solution was used for the titra-
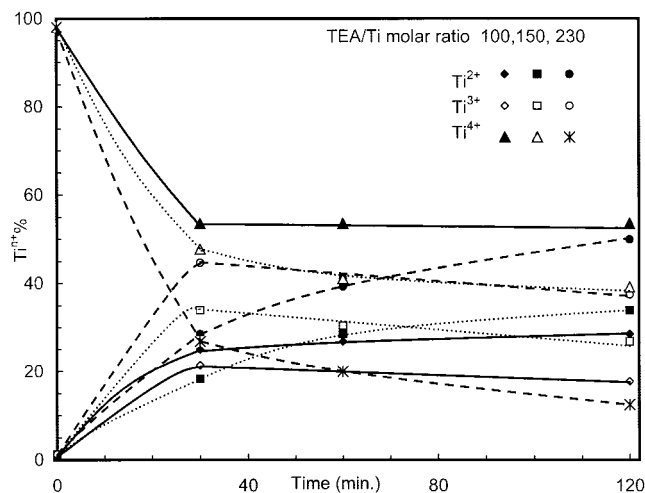
Figure 1 Titanium ions percentage–time profiles using MgCl$_2$/EB/TiCl$_4$–TEA catalyst system at various Al/Ti molar ratios.

tion in this procedure under argon atmosphere. In this titration Ti^{2+} species in the catalyst were oxidized by the protons as follows: $Ti^{2+} + H^+ \rightarrow Ti^{3+} + \frac{1}{2}H_2$. From this titration it was possible to calculate $[Ti^{2+}] + [Ti^{3+}]$.

From the values of titrations (A) and (B) it was possible to calculate the following: $[Ti^{2+}] = A - B$, $[Ti^{3+}] = 2B - A$, and $[Ti^{4+}] = [Ti^{n+}] - ([Ti^{2+}] + [Ti^{3+}])$.
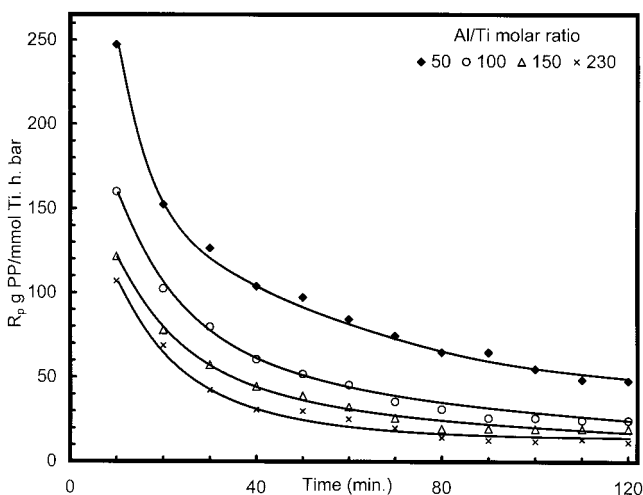
RESULTS AND DISCUSSION

Generally, by use of Ziegler–Natta catalyst systems for propylene polymerization, the reaction kinetics, the isotacticity of the produced polymer, and molecular weight are influenced by the nature of the alkyl aluminum and the Al : Ti molar ratio.

From the profiles, showing the relation between Ti^{n+} species percentage and time as in Figures 1 and 2, it can be seen that the highest percentage values of Ti^{3+} species were recorded in the first measurement after 30 min, after which Ti^{3+}% started to decrease gradually with time. The Ti^{3+} species percentage–time profiles, shown in Figures 1 and 2, almost correlate with the rate–time profiles of propylene polymerization shown in Figures 3 and 4, respectively, in which they both exhibited a steady-state decay type profile. The decrease in the Ti^{3+} species with time was accompanied by a decrease in the rate of polymerization. The Ti^{4+} species kept decreasing independent of the rate of polymerization, whereas the opposite was shown by the Ti^{2+} species, which kept increasing with polymerization time. Thus it would be reasonable to conclude that the Ti^{3+} species is more likely to be the active titanium species for the MgCl$_2$/EB/TiCl$_4$–AlR$_3$ catalyst systems during propylene polymerization.
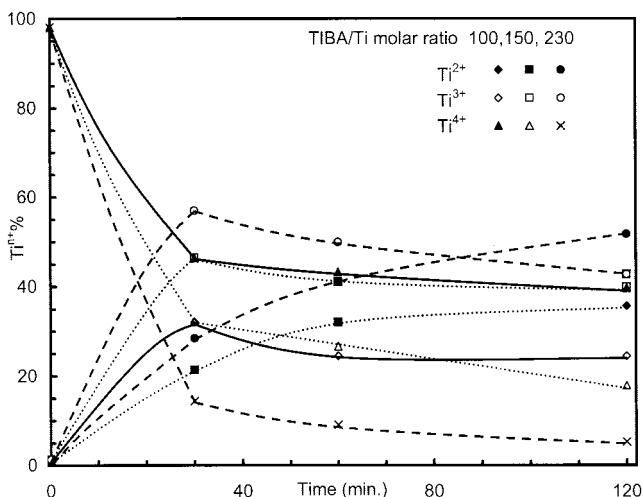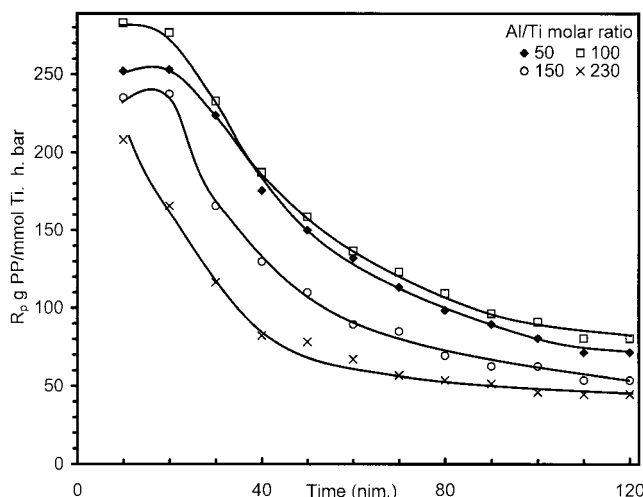
Figure 2 Titanium ions percentage–time profiles using MgCl$_2$/EB/TiCl$_4$–TIBA catalyst system at various Al/Ti molar ratios.

Figure 4 Polymerization rate–time profiles using MgCl$_2$/EB/TiCl$_4$–TIBA catalyst system at various Al/Ti molar ratios.

Catalyst deactivation with time may be attributed to different factors, which may vary from one catalyst system to another, as reported in the literature. The overreduction of Ti^{3+} species for some catalyst systems is one of those factors that can have a major effect in catalyst deactivation.[2,14] Keii et al.[15] reported that premixing of catalyst and cocatalyst ("catalyst ageing") reduced the activity of MgCl$_2$-supported type catalyst, which means that the cocatalyst has some role in catalyst deactivation. On the other hand, Keii et al.[15] suggested that the rapid decay of the polymerization rate may be attributed to the deactivation of the surface active sites by a strongly adsorbed cocatalyst species, which may lead to the reduction of Ti^{3+} to Ti^{2+}. Kohn et al.[16] used a mechanism, suggested by

Natta, that allows two principal interchanges of the catalytically active center, as shown in Scheme 1, where P is the polymer chain, (*) denotes a growing chain, and both $k(1)$ and $k(2)$ represent the corresponding rate constants for the two processes.

Increasing the Al : Ti molar ratio was found to cause an increase in the rate of polymerization up to a certain molar ratio, after which the rate started to decrease, as shown in Figures 3 and 4. However, increasing the Al : Ti molar ratio led to an increase in both species Ti^{3+} and Ti^{2+} and a corresponding decrease in Ti^{4+} species, as shown in Figures 1 and 2.

The decay in catalyst activity with an excess of alkyl aluminum could be attributable to an overreduction of the oxidation states of the active centers by the alkyl aluminum to lower oxidation state (lower than Ti^{3+}, usually Ti^{2+}). However, in this study trisobutylaluminum (TIBA) produced higher values of both polymerization rates and Ti^{3+} species compared with triethylaluminum (TEA).

It can be seen from Figures 3 and 4 that TIBA has a lower reducing ability than that of TEA, and thus a small amount of TEA was required to reach the maximum rate of polymerization. However, an increase in the Al : Ti molar ratio will increase the rate of overreduction of Ti^{n+} species, leading to a decay in catalyst activity.

In this study the catalyst system was aged by premixing the catalyst with two different types of cocatalysts, TEA and TIBA, for a period of 5 min. From Figure 5 it can be seen that the rapid decay in polymerization rate, which occurred within the first few minutes, corresponds to about 80% of the maximum catalytic activity. The catalytic activity after 40 min is about one quarter that of the unaged catalyst when using TIBA as cocatalyst, but reached a zero value

Figure 3 Polymerization rate–time profiles using MgCl$_2$/EB/TiCl$_4$–TEA catalyst system at various Al/Ti molar ratios.
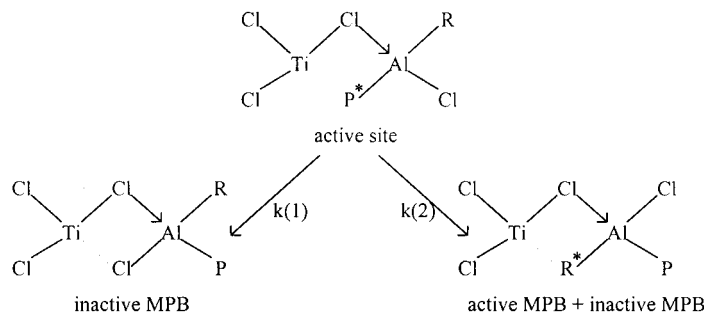
Scheme 1

when using TEA as cocatalyst, indicating that TEA, moreso than TIBA, is a stronger alkylating agent capable of overreducing Ti.

It may also be observed from Figure 5 that the overreduction of Ti^{n+} species occurred as the catalyst mixed with the cocatalyst. However, the absence of a monomer, which would compete with alkyl aluminum in reacting with the active centers, increased the overreduction of Ti^{n+} species.

In general, the alkyl aluminum must be adsorbed and diffused into the transition metal ion to form active metal–carbon bonds (alkylation of titanium). These reactions are then followed by a reduction of titanium oxidation states during which Ti^{n+} is reduced to a lower oxidation state.[1] Also an excess of alkyl aluminum causes a reduction in active center concentrations when the optimum ratio is exceeded.[11] Increasing the Al : Ti molar ratio initially causes an increase in the diffusion of alkyl aluminum into the support matrix, which facilitates the alkylation process of the potential active centers, leading to an increase in the initial rates of polymer formation, and causing fragmentation to occur at the earlier stage of

polymerization, consequently leading to an increase in the values of active centers. This also explains the reduction in the duration of the settling period.

Furthermore, it is believed that the nature and the morphology of the ball-milled catalyst support, in which active centers are located on the outer surface of the $MgCl_2$, would make the active sites more vulnerable to alkylation and deactivation by the alkyl aluminum.

It is well known that an increase in the Al : Ti molar ratio causes an increase in the overall rate of polymerization, up to a maximum value, after which the rate becomes independent or decreases with a further increase in alkyl concentration.[17–23] Tait et al.[23,24] suggested that the decrease in the polymerization rate above this maximum value may be attributed to the presence of excess alkyl aluminum competing with the monomer molecules for complex formation with active sites. It was also concluded that an increase in cocatalyst concentration causes an overreduction of the oxidation states of titanium ions. Kashiwa et al.[2] showed that the Ti^{2+} species polymerizes ethylene only, whereas the Ti^{3+} species polymerizes α-olefin. Kashiwa reported that pretreatments of catalyst with TEA result in a catalyst that is active only for ethylene polymerization. However, reoxidation of the catalyst with Cl_2 results in reactivating the catalyst for propylene polymerization. Soga et al.[14,25–31] established that Ti^{3+} species are active for the polymerization of both ethylene and propylene during copolymerization. However, further reduction of Ti^{3+} to Ti^{2+} results in polymerization of ethylene only.

Increasing the Al : Ti molar ratio of the cocatalysts used (TEA and TIBA) was found to cause a decrease in both the molecular weight and the isotactic index of the produced polypropylene. Figure 6 shows that TEA has a higher ability, than that of TIBA, to decrease both the molecular weight and isotactic index of the produced polypropylene. This might be attributed to the greater ability of TEA to reduce the oxidation state of titanium compared to that of TIBA.

The decrease in the molecular weight of the produced polypropylene, using a higher concentration of alkyl aluminum, is believed[23,32] to be attributed to the
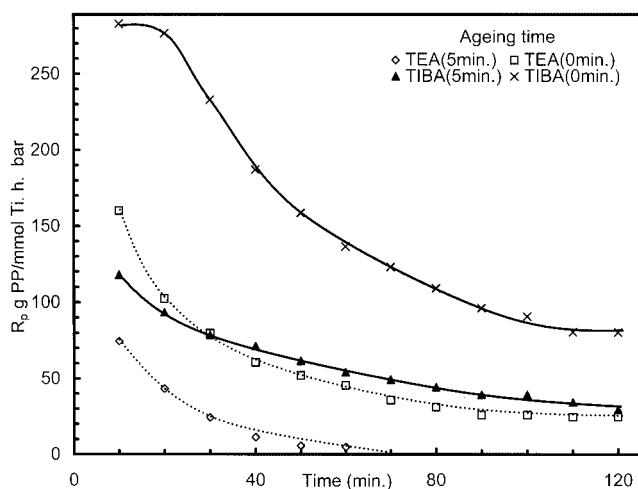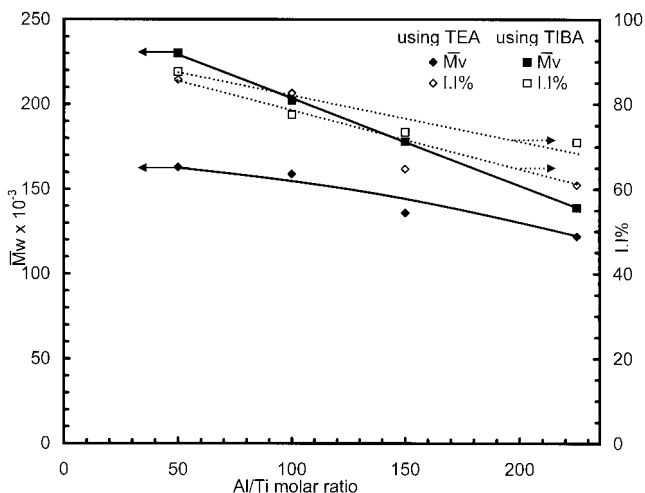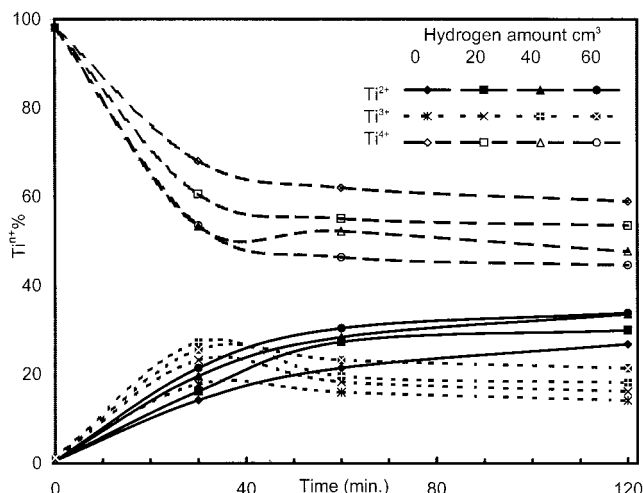

Figure 5 Polymerization rate–time profiles using unaged and aged $MgCl_2/EB/TiCl_4$ catalyst with TEA and TIBA at Al/Ti molar ratios of 100.

Figure 6 Viscosity-average molecular weights and isotactic index of produced polymers using MgCl$_2$/EB/TiCl$_4$ catalyst with TEA and TIBA at various Al/Ti molar ratios.

Figure 8 Titanium ions percentage–time profiles using MgCl$_2$/EB/TiCl$_4$–TIBA catalyst system with different amounts of hydrogen at Al/Ti molar ratio of 50.

increase in the amount of adsorbed alkyl aluminum species, which form a complex with the active Ti centers, leading to an increase in the rate of chain transfer, thus causing an overall reduction in the molecular weight.

In the present study, increasing the volume of hydrogen to 40 cm^3 caused a decrease in catalyst activity by 28%, as shown in Figure 7. However, considering the dilution effect of hydrogen addition and the lowering of monomer partial pressure in the system, the decrease in activity is, in fact, attributed to the dilution of monomer pressure by about 30%. Determination of titanium oxidation state showed an increase in both species Ti^{3+} and Ti^{2+} with a further increase in the volume of hydrogen added, as shown in Figure 8.

Despite the increase in Ti^{3+} species, there was no increase in activity, which may possibly be attributable to a significant increase in the inactive Ti^{2+} species, or to the differences in the activity of the various Ti active centers.

The present study shows that increasing hydrogen amount caused a decrease in both molecular weight and isotactic index of the produced polypropylene, as shown in Figure 9.

The effect of hydrogen in olefin polymerization has been investigated using different catalyst systems.[2,18,33–36] It is generally accepted that the main effect of hydrogen is that it acts as a chain-transfer agent, leading to a cleavage in the Ti—C bond, which
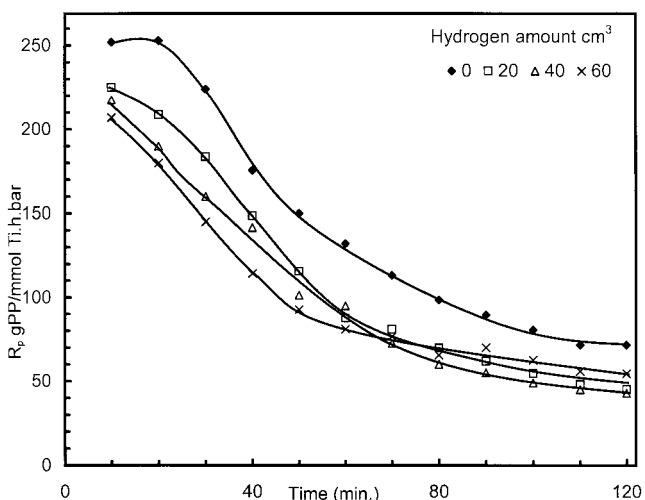
Figure 7 Polymerization rate–time profiles using MgCl$_2$/EB/TiCl$_4$–TIBA catalyst system with different amounts of hydrogen at Al/Ti molar ratio of 50.
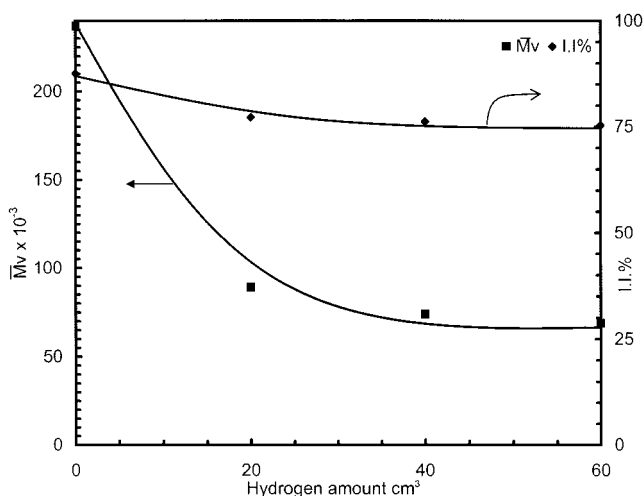
Figure 9 Viscosity-average molecular weights and isotactic index of produced polymers using MgCl$_2$/EB/TiCl$_4$–TIBA catalyst system with different amounts of hydrogen at Al/Ti molar ratio of 50.

produces a terminated polymer chain and a metal hydride species. This metal hydride center may then react with another monomer and either restart polymerization or remain as an inactive dormant site.

In some catalyst systems, rate enhancement has been observed after hydrogen addition to propylene polymerization.[33] In contrast to that, polymerization rate depression has been reported during ethylene polymerization,[34] as a consequence of the formation of inactive dormant sites.

Another investigator suggested that such behavior may be attributed to the morphology[11] of the catalyst, in which the catalyst's active sites, which are exposed on the outer surface of the catalyst particles, allow hydrogen in the polymerization medium to compete more effectively with the alkyl aluminum during the initial stages of the polymerization reaction. This results in the formation of metal–hydride bonds. Because the metal–hydride bond is less active than the metal–carbon bond toward propylene insertion,[15] the polymerization activity did not increase for the $MgCl_2/EB/TiCl_4$–TIBA catalyst system. In another possibility, hydrogen may complex with the metal–hydride bonds, subsequently causing competitive inhibition.[36] Many authors[37–40] have reported the fact that hydrogen causes a chain-transfer reaction, leading to a decrease in the polymer molecular weight.[39,40]

CONCLUSIONS

From this study we can generally conclude that, for the $MgCl_2/EB/TiCl_4$–AlR_3 catalyst-type systems, Ti^{3+} is believed to be the active site for propylene polymerization, given that Ti^{3+}% determinations by redox titration have shown that Ti^{3+} increases to a maximum in the first 30 min of the polymerization, followed by reduction in Ti^{3+} content, similar to the catalyst's rate–time profile.

We can also conclude from this study that the Ti^{2+} ion most likely is not an active metal species for propylene polymerization because its percentage increase, at all times, promotes a decrease in catalyst activity.

We should also note that the total amount of Ti^{3+} in the $MgCl_2/EB/TiCl_4$–AlR_3 catalyst systems is not the total amount of the active sites because this total amount includes an abundance of dormant Ti^{3+} sites that are inactive for propylene polymerization and, according to some studies[11,12] that determined the amount of active sites by C^{14} labeling, the active Ti^{3+} sites can be no more than 10% of the total Ti^{3+}.

It is also generally accepted that the active sites are usually exposed on the outer surface of the catalyst particles in which hydrogen will compete more effectively with the alkyl aluminum during the initial stages of the polymerization reaction.

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