

Polymerization of Olefins through Heterogeneous Catalysis. XII. The Influence of Hydrogen in the Solution Copolymerization of Ethylene

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SYNOPSIS

The copolymerization of ethylene with highly active $\text{TiCl}_4/\text{MgCl}_2$ -supported catalysts in solution reactors at 185°C and 400 Psig pressure is presented. The performance of these supported catalysts at these conditions is characterized by a high initial rate that decays rapidly within the 10 min polymerization period. In the presence of hydrogen and a comonomer, catalyst yields up to about 300 kg/g (Ti) are achieved. The kinetic data indicate rate enhancement when hydrogen is added in moderate concentrations. However, a high concentration of hydrogen results in a decreasing rate of ethylene consumption. Increasing the H_2/C_2 molar ratio in the range $0\text{--}10.66 \cdot 10^{-3}$ leads to a reduction in the M_n values from 31,600 to 17,400. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the polyolefin industry, the solution process is one of the oldest processes for the synthesis of Ziegler–Natta polymers. The first low-pressure polyethylene plants constructed in the late 1950s were solution-process plants.¹ Details of the streamlined solution processes are very scarce in the literature^{2,3}; however, some information about the DuPont process has been described by Forsman.⁴ The Dow solution process has been reported to resemble the DuPont process.⁵ In all solution processes, the temperature is sufficiently high so that the polymer is in solution. However, in some solution processes, the catalyst is homogeneous, whereas in others, the catalyst is on a heterogeneous support. The latter case is investigated in this paper.

Solution-polymerization processes have some unique advantages over slurry- or gas-phase polymerization in that the polydispersity, M_w/M_n , can be better controlled and the process variables are also more easily controlled because of the homogeneous polymer phase. Short residence times, high

polymerization temperatures, and moderately high pressures are the main characteristics of the solution process. The highest molecular weight products are not produced easily at such high temperatures. The solution process is therefore most suitable for the production of lower molecular weight (high MI) resins, which are difficult to produce in the slurry- or gas-phase processes.⁶ The high reaction temperature leads to high reaction rates and high polymer yields. Also, in solution polymerization, it is feasible to separate the bulk of the solvent from polyethylene by fast solvent evaporation after the pressure decrease. This makes it possible to produce polyethylene granules immediately after the polymer melt leaves the reactor. Because of the short residence time and high polymer concentrations, relatively small reactors can be employed, and multiple reactors can be used in series or parallel to alter the polydispersity index; thus, a broad range of products can be made in a single plant. The process can be used for the production of HDPE and LLDPE without demanding fundamental changes in reactor design.^{1,7}

Using low-activity catalysts in the early days of the Ziegler-catalyzed polymerizations resulted in relatively poor plant efficiency; energy requirements were costly and monomer and solvent losses were high. However, today, high-activity Ti-supported

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catalysts produce high yields, thus eliminating the costly steps of catalyst residuals removal. Reaction temperatures have been increased, thus permitting operation at higher polymer concentration; also, polymer recovery by devolatilization was developed to eliminate the high cost of steam stripping. To achieve these improvements, the catalysts used in the solution process must be able to withstand these higher reaction temperatures.

Kinetic studies on the solution polymerization of olefins are relatively scarce in the scientific literature compared to studies on gas- or slurry-phase polymerizations. Thus, in this series of papers, we present a detailed study of the kinetics and resulting polymer properties for ethylene copolymerization over a high-activity $\text{TiCl}_4/\text{MgCl}_2$ -supported catalyst. In this paper, we present the effect of hydrogen, and in the next three papers of this series, we provide a study on the effects of comonomer and solvent, the effects of reaction temperature, and the effects of reaction pressure.

In Ziegler-Natta-catalyzed polymerizations with titanium-based catalysts, hydrogen is the most effective and widely used molecular weight regulator. Hydrogen is inexpensive, is easy to use and does not leave a residue in the polymer. Almost at the same time, Natta et al.,^{8,9} Hoechst,¹⁰ and Hercules¹¹ disclosed the use of H_2 to control the molecular weight

in Ziegler-Natta polymerizations. According to Natta et al.^{8,9} the chain termination involves the hydrogenolysis of the metal-polymer bond that would result in the formation of a transition-metal hydride. In reality, two major effects are encountered when H_2 is added to an olefin polymerization system. The first effect is controlling the molecular weight of the polymer by a chain transfer reaction. The other effect is a kinetic factor, and up to the present time, there is no comprehensive agreement on the exact influence of hydrogen on polymerization kinetics.¹² For example, one can find reports in the scientific literature of hydrogen enhancing the polymerization rate in some cases and, in other cases, reducing the rate of polymerization. Much of this controversy results from the fact that different polymerization systems, including the catalyst/monomer system, gas or slurry polymerization, monomer chain length, and polymerization conditions will interact in a different way with hydrogen.

Table I gives an overview of some of what has been published in the scientific literature on the hydrogen effect on gas- or slurry-phase ethylene or propylene polymerizations. In the upper part of Table I, the effect of hydrogen on polymerization activity has been reported using first-generation catalysts. In the lower part, highly active $\text{TiCl}_4/\text{MgCl}_2$ -supported catalysts were used. Examination of the

Table I Overview of H_2 Effect on Ethylene or Propylene Polymerization/Slurry or Gas Processes

| Catalyst System | C_2H_4 | C_3H_6 | Temp (°C) | Pressure (kg/cm ²) | Diluent | H_2 | Activity (g/g cat h) | Ref. |
|---|------------------------|------------------------|--------------|-----------------------------------|---------------|-----------------------|-------------------------|------|
| $\delta\text{-TiCl}_3 \cdot \frac{1}{3}\text{AlCl}_3$ — AlEt_3 — AlEt_3 | Yes | | 35 | 0.4 | Nil | 0 | 19 | 13 |
| | | | | | | 0.2 atm | 9 | |
| | Yes | | 30 | 2 | Toluene | 0 | 23 | |
| $\delta\text{-TiCl}_3 \cdot \frac{1}{3}\text{AlCl}_3$ — Et_2AlCl | | Yes | 70 | 4 | Nil | $9.10^{-4} M$ | 12 | 14 |
| | | | | | | 0.6 atm | 1500 | 15 |
| | | Yes | 70 | 4 | Heptane | 0 | 2000 | 95 |
| | | | | | | $1.5 \cdot 10^{-3} M$ | 90 | 16 |
| (kg/g Ti h) | | | | | | | | |
| $\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3$ | Yes | | 60 | 3 | Hexane | 0 | 177 | 17 |
| | | | | | | 1.0 bar | 171 | |
| $\text{Mg}(\text{OR})_2/\text{TiCl}_4/\text{AlEt}_3$ | Yes | | 85 | 6 | Diesel oil | 0 | 611 | 18 |
| | | | | | | 7 vol % | 499 | |
| $\text{TiCl}_4/\text{MgCl}_2/\text{AlEt}_3$ | | Yes | 70 | 3 | Hexane | 0 | 36.6 | 17 |
| | | | | | | 1.2 bar | 112 | |
| $\text{Mg} - \text{Ti} - \text{Cat}/\text{AlEt}_3$ | | Liquid pool | 70 | 31 | — | 0 | 565 | 19 |
| | | | | | | 1.0 bar | 647 | |

data collected in Table I and elsewhere^{20,21} reveals that, for low- and high-activity catalysts, hydrogen usually results in decreasing the polymerization activity in ethylene polymerization and increasing the activity in propylene polymerization. It should be emphasized at this point, however, that the data collected in Table I are for gas- or slurry-phase olefin polymerizations. The operating conditions of these processes are somewhat moderate when compared with a temperature of 185°C and pressure of 400 Psig employed in the present investigation for ethylene polymerization in solution. Because of the complexity of olefin-catalyzed polymerization, it is difficult to compare data obtained under different reaction conditions. Various factors can influence the outcome of the H₂ addition to a polymerization system, e.g., the nature of the aluminum alkyl compound, the Al/Ti ratio, the monomer, temperature, and pressure. In particular, the nature of the aluminum alkyl and the Al/Ti mole ratio determine the relative population of the titanium oxidation states (Ti = 4+, 3+, and 2+). It has been reported that transfer reactions occurring by hydrogenolysis of the metal-polymer bonds take place only on Ti³⁺, whereas Ti⁴⁺ promotes only an exchange between added H₂ and the hydrogen atom on the β-carbon of the polymer chain.²²

Employing a TiCl₄/MgCl₂-AlEt₃-catalyst system in propylene polymerization, Guastalla and Giannini¹⁷ found that the initial rate increases strongly with increasing H₂ pressure. Hydrogen was found to appreciably slow down the catalyst decay. However, above an optimal [H₂], a reduction in catalyst activity was reported. By contrast, in the polymerization of ethylene, a deactivating effect was observed.¹⁷ In a seeming contradiction, Soga and Siono²³ observed a decrease in the catalytic activity for propylene polymerization with an increase of H₂ partial pressure. This has been attributed to a decrease in the concentration of active centers, [C*], due to the slow "realkylation" of the Ti-H bond by the monomer. However, the data obtained by Soga and Siono refer to the predominantly stereospecific polymerization of propylene. Guastalla and Giannini¹⁷ reported that above the optimal hydrogen level the yield of the stereoregular heptane-insoluble polypropylene fraction decreases substantially. The hydrogen would, therefore, have a different effect depending on the nature of the active site involved in the polymerization. Using a TiCl₄/MgCl₂/diethylphthalate/hexyltriethoxysilane/AlEt₃ catalyst system, Kashiwa and Kioka²⁴ recently reported that H₂ resulted in about threefold increase in the activity

of propylene or butene homopolymerization, whereas no such enhancement was observed in case of ethylene polymerization. The number of active centers and *k_p* were determined by kinetic methods; the authors reported that there was no change in [C*], but *k_p* was higher in the case of H₂. Therefore, Kashiwa and Kioka concluded that the activity enhancement in the presence of H₂ was due to higher *k_p* values. From this discussion, it is clear that the effect of H₂ on the reaction mechanism is complex and needs further study.

EXPERIMENTAL

Materials

The high-activity TiCl₄/MgCl₂ catalyst used in this study was supplied by Dow Chemical USA, Freeport, TX. Polymer-grade ethylene, 99.5% purity; ultra-high purity nitrogen, 99.999%; and hydrogen, 99%, were purchased from Matheson Gas Products. 1-Octene, 99%, was purchased from Sigma Chemical Co., and 1-hexene, 99%, from Alfa Products. Anhydrous calcium hydride, 40-mesh, was supplied by Aldrich Chemical Co. Antioxidant, Irganox 1010, was obtained from Ciba-Geigy Corp. HPLC grade isooctane (2,2,4-trimethylpentane) was purchased from VWR-Scientific and isopar-E, a mixture of C₈-C₉ isoparaffinic hydrocarbons, was supplied by Exxon Chemical Co. The liquid comonomers, 1-octene and 1-hexene, and solvents for polymerization (isooctane or isopar-E), were purified by stirring overnight over anhydrous CaH₂ and then vacuum-distilled. The distillate is collected over dry molecular sieves and purged with dry nitrogen before use.

The Polymerization System

The system designed for the copolymerization of ethylene/linear α-olefins is shown schematically in Figure 1. The reactor is a 1-L Autoclave Engineers equipped with a magnidrive stirrer. A power unit is used for controlling the stirring speed and the external jacket heater. The gas lines connected to the reactor consist of two nitrogen lines (high and low pressure), hydrogen, ethylene, and propylene or 1-butene. The gases are purified before admission to the reactor by passing through three drying columns consisting of molecular sieves, activated alumina, and a (copper oxide) BASF catalyst, respectively. The reactor top cover has seven openings: two dip-tubes for liquid and gas injections, a thermowell

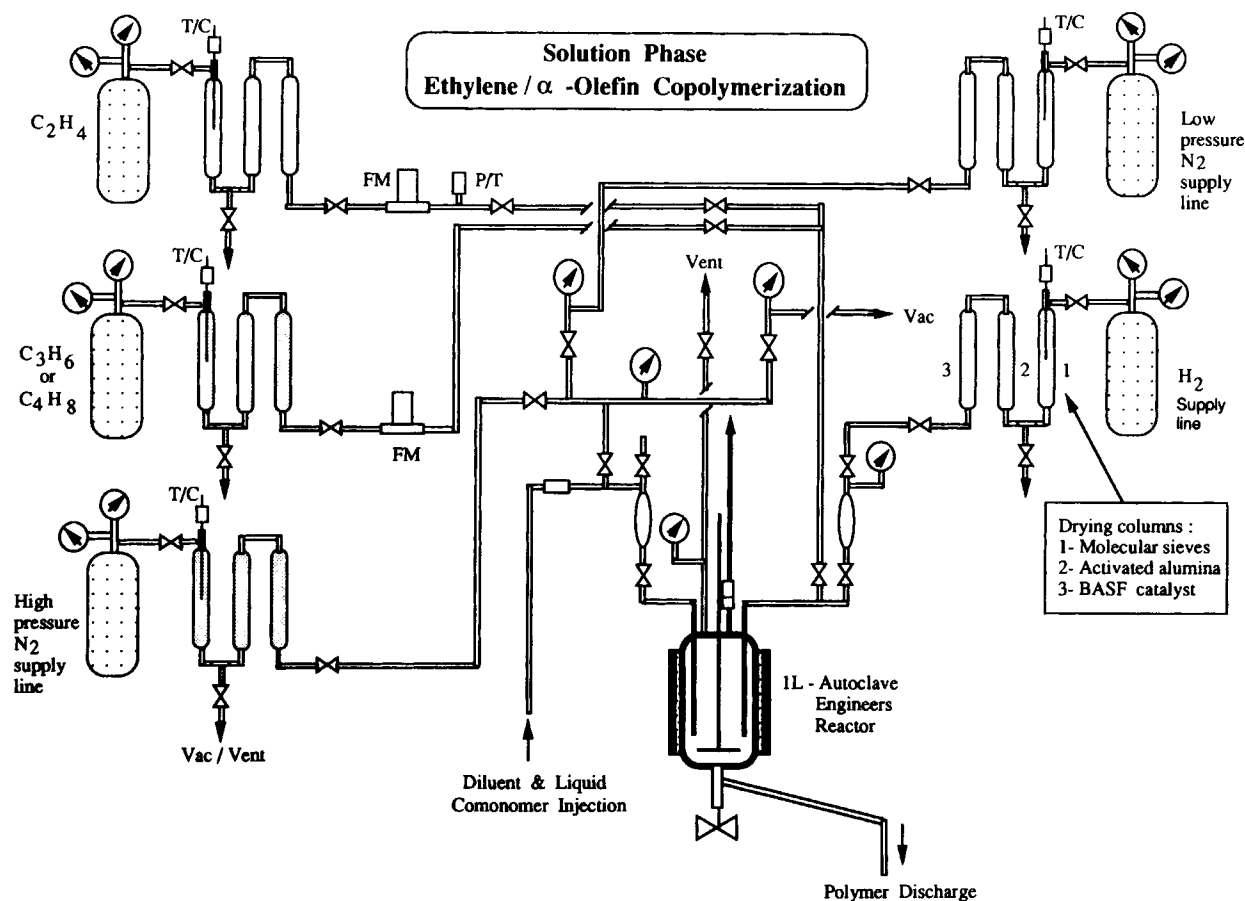


Figure 1 Schematic presentation of the system designed and used of ethylene copolymerization in the solution phase.

dipped in the liquid phase for temperature monitoring, a vent line, a rupture disc connection, and a sample valve. In addition, an opening for a fiber optics stainless-steel probe for near-infrared studies is also available to use in monitoring the polymer solution spectra during polymerization.

Polymerization Procedure

The polymerization is conducted in a semibatch mode. Ethylene pressure is maintained constant by using a pressure regulator and is supplied on demand. The flow of ethylene in *slpm* is measured using a Teledyne-Hastings mass flowmeter. Reactor temperature and pressure, ethylene pressure, and flow rate are monitored using display units that are connected to a computer for data acquisition. During polymerization, a measurement of pressure, temperature, and gas flow rate is recorded every 5 s.

A typical polymerization run is carried out as follows: The dry reactor, at about 80–90°C, is flushed with nitrogen several times and then left under low

N_2 pressure (~ 2 Psig). A 500 mL glass bottle containing a predetermined quantity of the solvent, and a liquid comonomer if desired, is then connected to the catalyst bomb using a quick-fit connection. The solvent is transferred to the reactor, through the catalyst bomb, using low nitrogen pressure (5–6 Psig). A small quantity of hydrogen is then admitted to the reactor using the hydrogen stainless-steel bomb (volume = 75 cm³, 0–60 Psig H_2). The reactor temperature is then raised to the desired temperature using the external electrical heater; simultaneously, ethylene is supplied slowly so that the desired reactor temperature and total pressure (e.g., 185°C and 400 Psig) are reached at about the same time. When the reactor temperature and pressure have stabilized, the cocatalyst solution and the catalyst slurry are transferred separately, under a low N_2 flow, to the catalyst bomb using preheated N_2 flushed, gas-tight glass syringes fitted with stainless-steel needles. High-pressure N_2 (~ 600 Psig) is then used to inject the catalyst/cocatalyst mixture in the solvent phase. The total liquid volume (solvent, co-

monomer, catalyst, and cocatalyst solution) in the reactor is kept at 400 mL and the polymerization time is 10 min.

At the end of the polymerization period, the ethylene flow is switched off and the reactor pressure is used to flush the hot polymer solution slowly through the reactor bottom flush valve. The polymer solution passes through a 140°C preheated 0.5 in.-diameter stainless-steel line to an oxygen-free vessel (containing about 0.1 g Irganox 1010 antioxidant), equipped with a vent. The polymer is recovered by solvent evaporation. Figure 2 shows a schematic presentation of the reactor top cover connections for the catalytic components injection and the polymer collection unit.

Thermodynamic data²⁵ for the estimation of ethylene, comonomer, and H₂ concentrations in isooctane or isopar-E have been obtained using the

ChemCad databank. This is based on the Soave-Redlich-Kwong equation. Hydrogen concentrations, hydrogen/ethylene, and ethylene/1-octene molar ratios in the liquid phase are presented in Table II. Molecular weight analyses have been performed on GPC at 135°C; trichlorobenzene was used as the solvent. FTIR, corrected by NMR, was used for the determination of branch content and comonomer incorporation.²⁶

RESULTS

The hydrogen effect on the ethylene consumption rate in ethylene/1-octene copolymerization is shown in Figure 3. The lowest $R_{p(max)}$ and the fastest decay are observed to occur when no hydrogen was used. Upon the introduction of a small amount of H₂ (low

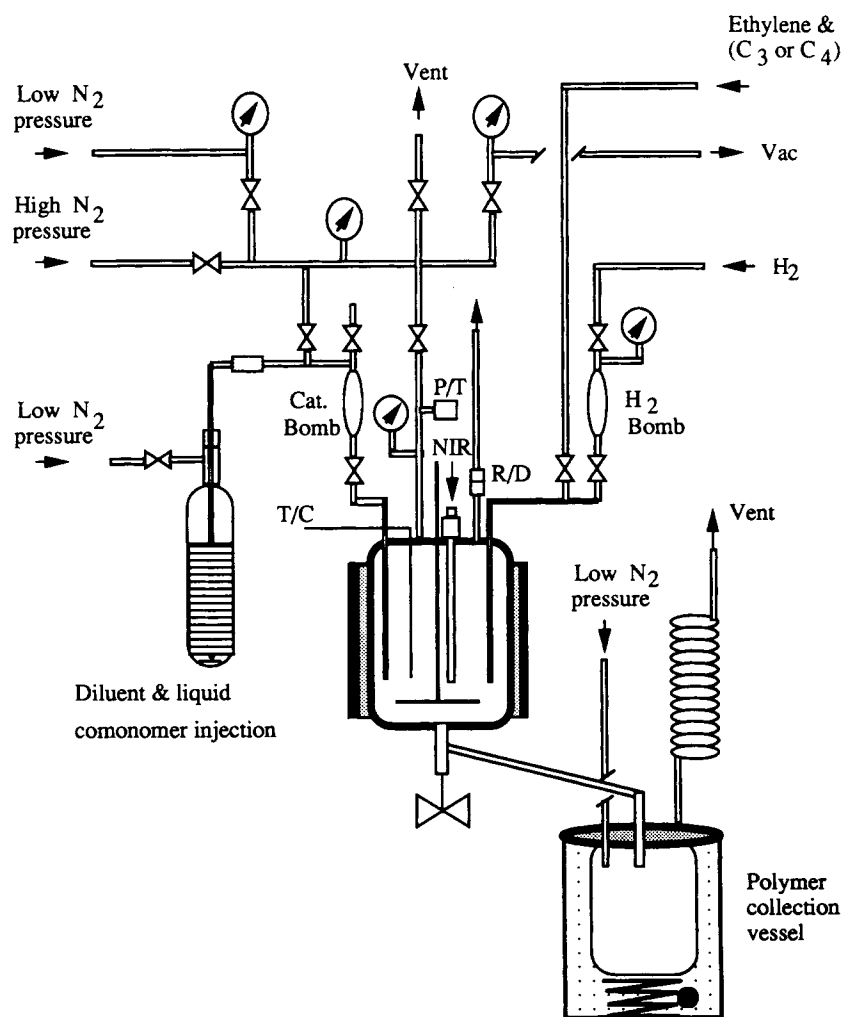


Figure 2 Schematic presentation of the reactor top cover connections and the polymer collection vessel. P/T = pressure transducer, R/D = rupture disc, T/C = thermocouple, and NIR = near infrared fiber optics probe (stainless steel).

Table II Concentration of Hydrogen, Hydrogen/Ethylene, and Ethylene/1-Octene Molar Ratios in the Liquid Phase (Isooctane)

| $10^3 \cdot [H_2]$ (mol/L) | $10^3 \cdot H_2/C_2$ (Molar) | C_8/C_2 (Molar) |
|-------------------------------|---------------------------------|----------------------|
| — | — | 0.2687 |
| 2.813 | 3.481 | 0.2722 |
| 5.618 | 7.033 | 0.2756 |
| 7.017 | 8.838 | 0.2775 |
| 8.414 | 10.659 | 0.2793 |

Conditions: Total initial solvent volume, including comonomer, = 400 mL; 400 Psig total pressure; 185°C.

H_2/C_2 ratio) in the polymerization system, an increase in the initial $R_{p(max)}$ is observed and the decay in the polymerization rate is improved. There is a continuous increase in $R_{p(max)}$ with increasing the H_2/C_2 ratio; however, at the highest H_2/C_2 ratio, the decay in the polymerization rate becomes more significant.

The rate-time profiles presented in Figure 3 show a remarkable high initial peak in the polymerization rate that decays rapidly within the short 10 min polymerization time. This is the result of using a high-activity $TiCl_4/MgCl_2$ -supported catalyst coupled with high polymerization temperature: 185°C. This shape of the rate-time profile is a characteristic of all the polymerizations carried out in solution co-

polymerization of ethylene in the present investigation. Lower initial peaks and less rapid decay were, however, observed at lower polymerization temperatures.²⁷ The cumulative reactor yield as a function of H_2/C_2 ratio is shown in Figure 4. A sharp increase in the polymerization yield is observed until an optimal H_2/C_2 ratio is attained, beyond which a decrease in the yield occurs.

The conclusion that can be drawn from Figures 3 and 4 is that H_2 accelerates the kinetic rate when used in moderate concentration. This indicates that H_2 is participating in the creation of new centers or removing bulky chains attached to the polymerization centers by a chain transfer reaction. The other effect that can be seen in Figure 3 is that even though the highest initial $R_{p(max)}$ was obtained at the highest H_2/C_2 used, the decay in R_p was the most significant, indicating that H_2 enhances deactivation when used in excess.

The effectiveness of hydrogen in reducing both weight-average and number-average molecular weight of an ethylene/1-octene copolymer is illustrated in Figure 5. Within the range of the H_2/C_2 molar ratio used, the M_w has dropped by a factor of about 2.4 and M_n by a factor of about 1.8. As stated earlier, H_2 reduces the polymer molecular weight by transfer reaction. Zakharov et al.²⁸ and Grievson¹⁴ established that the rate of chain transfer to H_2 was substantially higher relative to chain transfer to olefin or to the aluminum alkyl compound.

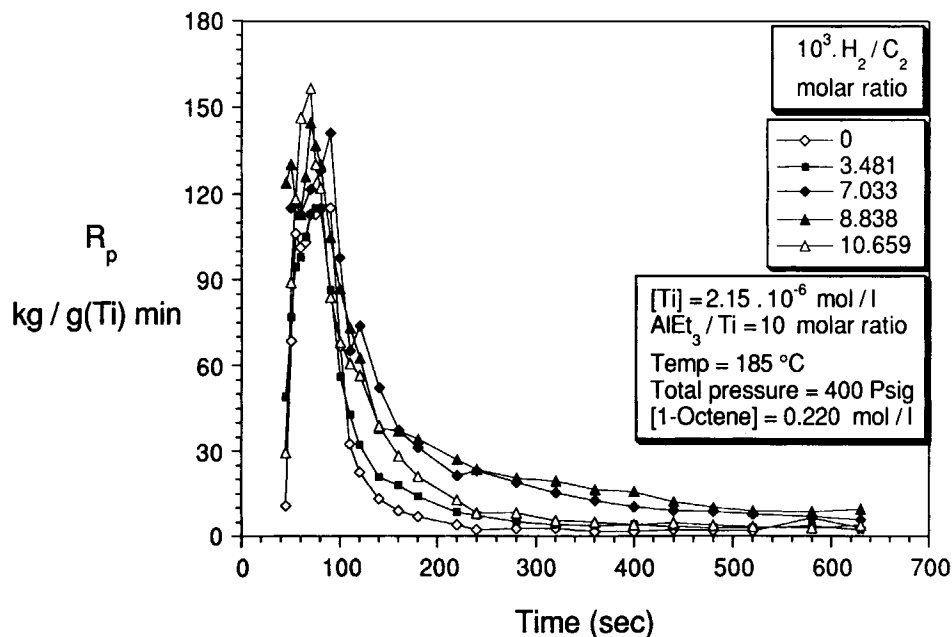


Figure 3 Effect of H_2/C_2 molar ratio ($[H_2]$ variation) on the ethylene consumption rate in C_2/C_8 copolymerization. Solvent = isooctane.

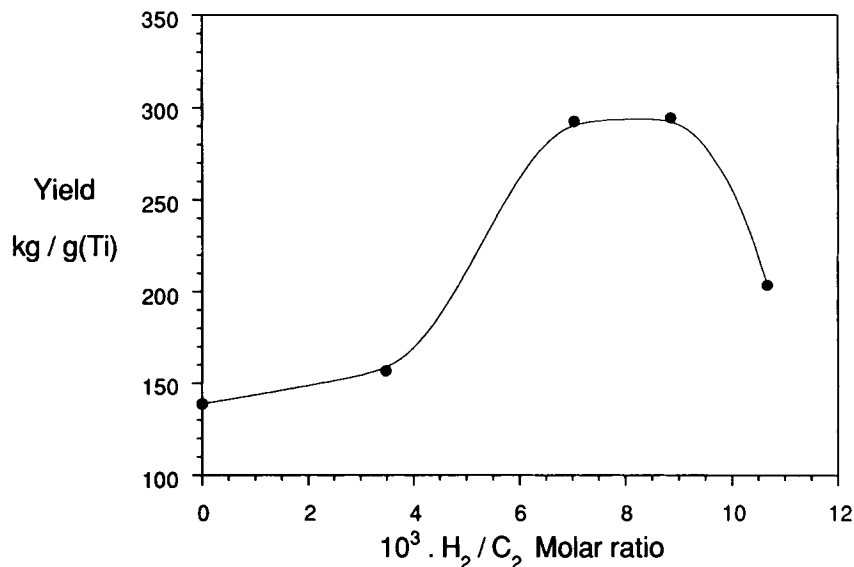


Figure 4 Effect of H_2/C_2 molar ratio variation on the polymerization yield in C_2/C_8 copolymerization. Conditions as in Figure 3.

Diverse effects of H_2 on the polydispersity of polyolefins have been reported. H_2 has been reported to narrow²⁹ or broaden^{30,31} the polydispersity of polyethylene or polypropylene or causes negligible changes.^{32,33} The data available are inadequate to draw any general conclusion. Most studies used H_2 in batch. This could cause broadening of the polydispersity due to a changing H_2 /olefin ratio over the course of polymerization when a long polymerization time is used. Keii³⁴ suggested that hydrogen is not expected to cause a significant change in the poly-

dispersity. In the present investigation, the range of the H_2/C_2 ratio used resulted only in a moderate drop in the polydispersity, M_w/M_n , with increasing the H_2 concentration. Figure 6 shows that the polydispersity of an ethylene/1-octene copolymer is in the range 3–4 for all hydrogen levels.

The effect of hydrogen on the extent of comonomer incorporation in the polymer chain is shown in Figure 7. Two observations can be made: First, for the conditions studied, the amount of octene incorporated into the polymer chain is rather small, i.e.,

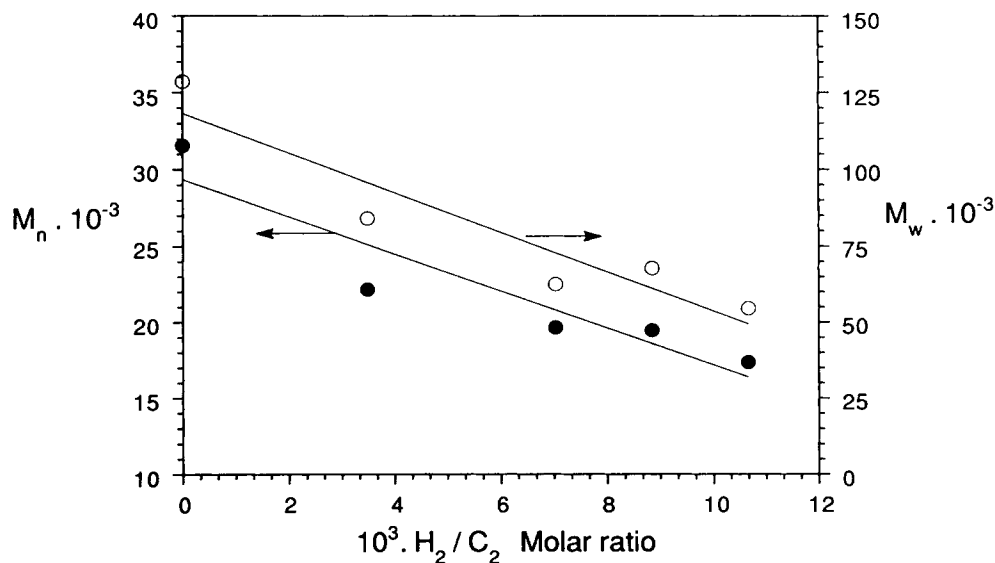


Figure 5 H_2/C_2 molar ratio variation effects on M_n and M_w in C_2/C_8 copolymerization. Conditions as in Figure 3.

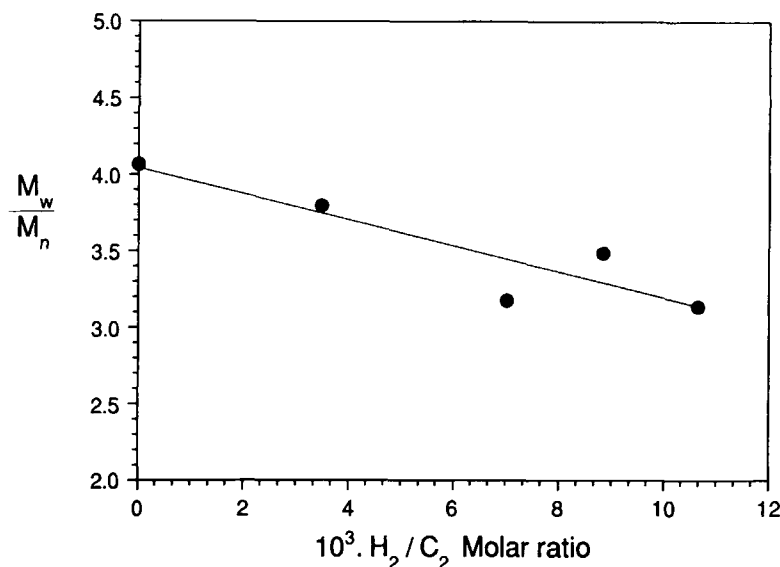


Figure 6 H_2/C_2 molar ratio variation effect on the polydispersity index, M_w/M_n , in C_2/C_8 copolymerization. Conditions as in Figure 3.

about 1.5 mol %. Second, hydrogen has a small effect on the 1-octene incorporation in the polymer chain, ranging from 1.4 to 1.7 mol %. The branching content (given as $CH_3/1000 C$) in the copolymer is related to the mol % comonomer incorporated. The branch content dependence on the H_2/C_2 molar ratio is shown in Figure 8. It can be seen that the branch content also tends to increase only to a small extent with increasing H_2/C_2 ratio, and it varies in the range 6.5–8.0 methyl groups per 1000 C atoms.

DISCUSSION

Effect of Hydrogen on the Polymerization Rate

A characteristic feature of $TiCl_4/MgCl_2$ -supported catalysts in olefin polymerization is that the rate of polymerization decays with increasing polymerization time. The decay extent is dependent on the reaction conditions and the particular catalyst system used. The data presented in the present study show

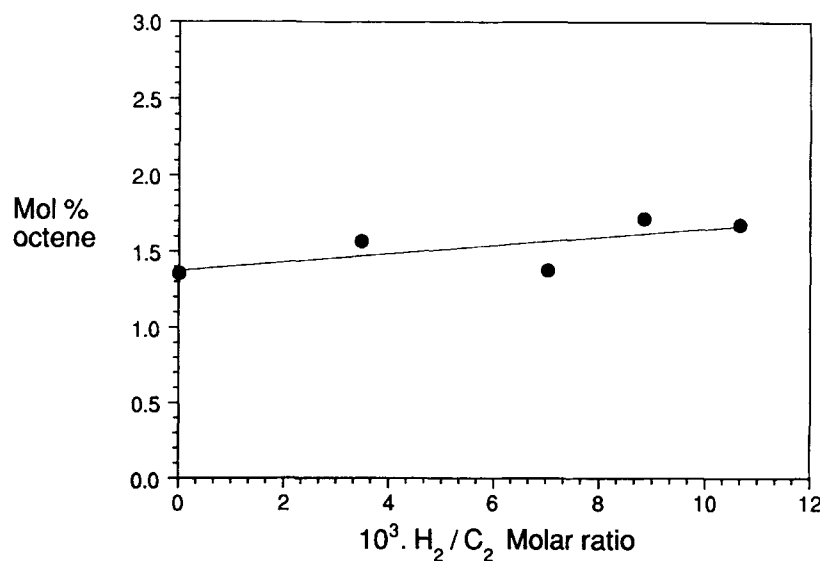


Figure 7 H_2/C_2 molar ratio variation effect on the mol % 1-octene incorporation. Conditions as in Figure 3.

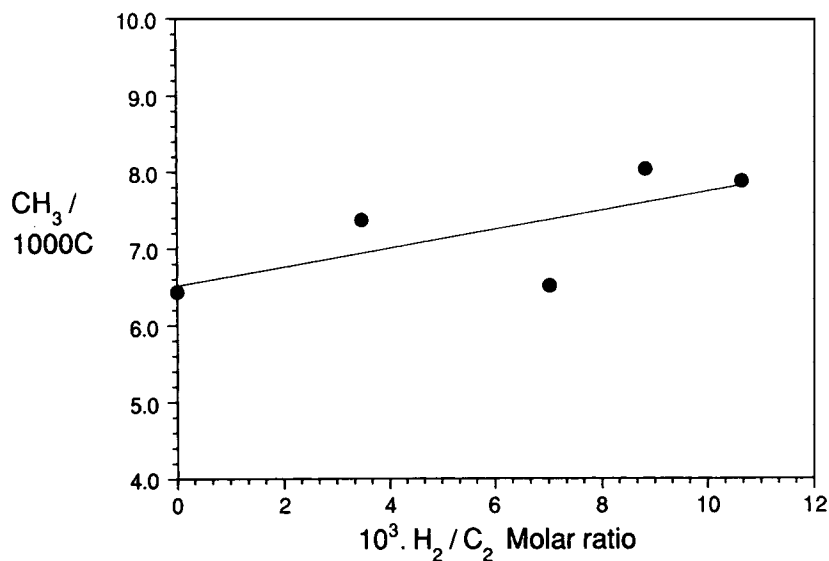


Figure 8 H_2/C_2 molar ratio variation effect on the branch content in C_2/C_8 copolymerization. Conditions as in Figure 3.

that the decay in the polymerization rate is quite severe due to the high-activity-supported catalyst used and the severe reactor conditions. Many authors in this field have analyzed the decay rates in olefin polymerizations. Different decay rate laws have been proposed to account for the deactivation of the rate with time. A first-order model has been employed by Galli et al. for the polymerization of propylene in hexane solvent using a $TiCl_4/MgCl_2$ -based catalyst.³⁵ A second-order decay rate law has been proposed by Doi et al.³⁶ for gas-phase polymerizations of polypropylene. Brockmeier and Rogan³⁷ analyzed the decay kinetics of propylene polymerization using first-order, 1.5-order, and second-order rate laws; the authors suggested that the 1.5-order decay model provides an accurate correlation from 2 to 15 h of polymerization duration. Tait and Wang,³⁸ using a $TiCl_4/MgCl_2$ -based catalyst for propylene polymerization, analyzed the decay in the polymerization rate with time and suggested that the decay can be better described by a modified multicenter first-order decay model.

The rate-time profiles reported on the solution copolymerization of ethylene in the present study show a remarkably high initial rate of polymerization that decays quite rapidly within the short 10 min polymerization period. An attempt to fit the rate decay to first-order kinetics is made by using the rate law in eq. (1):

$$R = R_{\infty} + (R_{\max} - R_{\infty})e^{-k_d(t-t_{\max})} \quad (1)$$

where t_{\max} is the time at peak rate, R_{\max} .

Figure 9 shows plots according to eq. (1) for the rate-time profiles obtained when the H_2/C_2 molar ratio was varied (see Fig. 3). It can be seen that fitting of the rate-time profile to a first-order decay rate law is reasonably well represented by the above law.

The conclusion that can be drawn from the rate data in the present study is that moderate amounts of H_2 accelerate the rate at short times so that R_{\max} increases (cf., Fig. 3) and hinders deactivation at longer times (cf., Fig. 9). At higher H_2 levels, the rate deactivation increases. The rate acceleration could result from a number of factors in the present system, i.e., the creation of new polymerization centers or activating of a dormant site. Another likely possibility is cleaning up a blocked or a slow propagating center due to bulky polymeric chains by a chain transfer reaction. Another significant effect is that the main reaction of hydrogen is to lower the polymer molecular weight by a chain transfer reaction. This would result in a lower polymer solution viscosity. Because of the very high initial rise in the polymerization rate, it is expected that the transfer of ethylene from the gas to the solution would be mass-transfer-limited. Thus, the reduced solution viscosity at higher H_2 levels would enhance mass transfer and increase the concentration of ethylene in the solution.

At the highest H_2/C_2 used, the decay in R_p was the most significant, indicating that H_2 also promotes deactivation when used in excess. The reduction in the activity can result from excess chain transfer reactions and competition with the $AlEt_3$

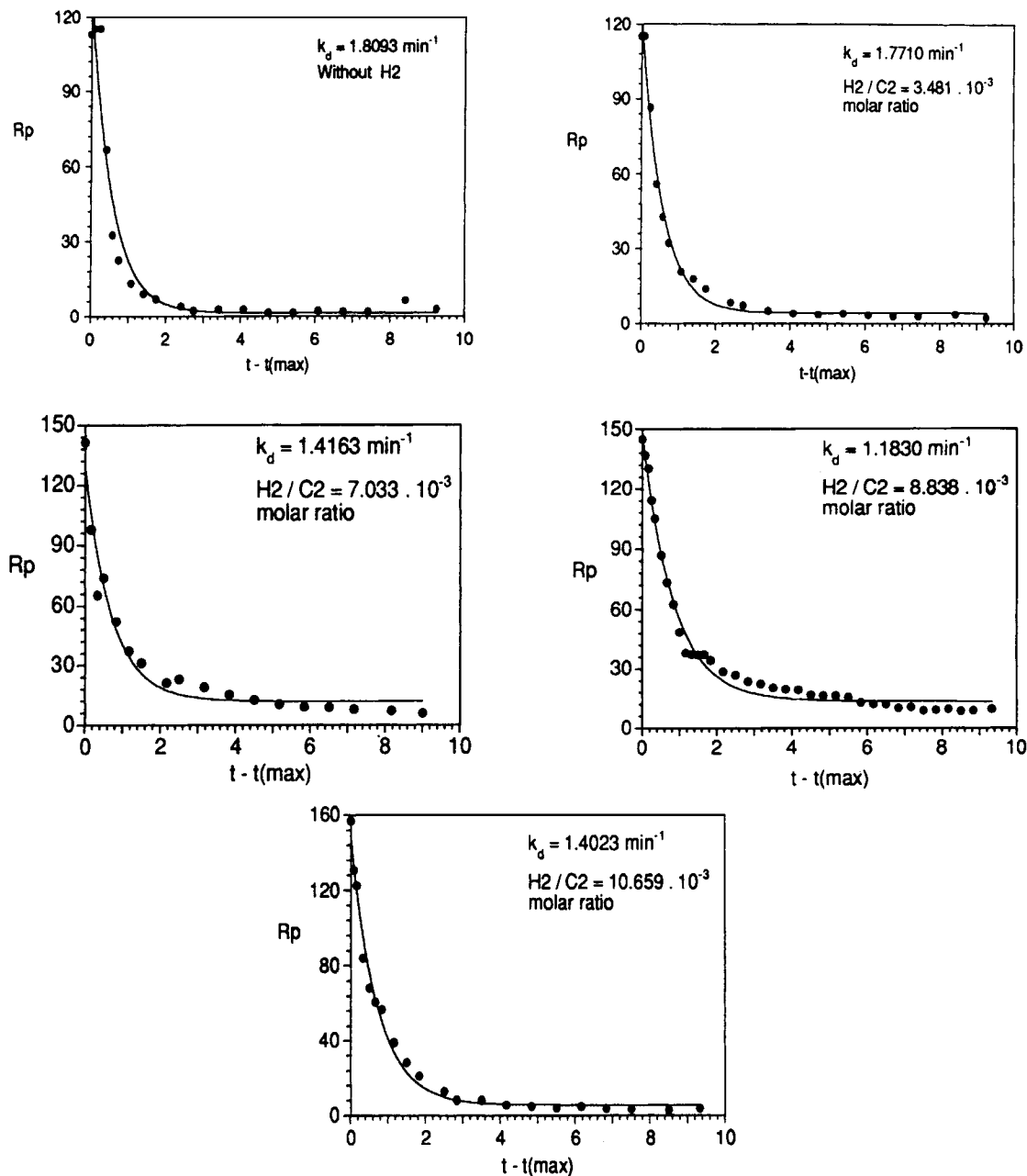
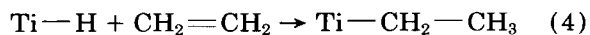
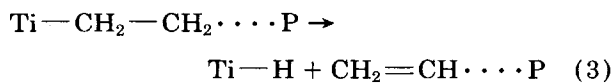
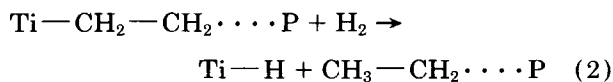


Figure 9 Plots of R_p vs. $t - t_{(max)}$ according to eq. (1) for different H_2/C_2 molar ratios in C_2/C_3 copolymerization. Conditions as in Figure 3.

and monomer(s) for adsorption. Moreover, hydrogen is known to interact with aluminum alkyls. In case where $AlEt_3$ is used, $AlEt_2H$ may form. This may result in lowering the activity through side reactions.

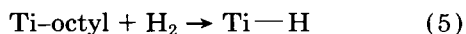
It is well known that hydrogen reduces the polymer molecular weight by a hydrogenolysis mechanism, thus generating a transition-metal hydride bond [eq. (2)]. In addition, a $Ti-H$ bond can result from a β -hydride elimination reaction [eq. (3)]:



The main reason that has been put forward by Natta et al.^{8,9} for the reduction in the ethylene po-

lymerization activity in the presence of H_2 , is that the "realkylation" of the Ti—H species by ethylene was hypothesized to be a slow process, i.e., eq. (4). This would reduce the rate at higher hydrogen concentrations.

Using a $TiCl_3/AlEt_2Cl$ catalyst system for the polymerization of propylene, Ross¹⁵ suggested that H_2 exerts a double effect on the catalytic activity. Atomic hydrogen would inhibit the polymerization rate, whereas molecular hydrogen, especially at high monomer and H_2 concentrations, would create additional active centers, thus increasing the polymerization rate. Potkov³⁹ also found an activating effect of H_2 during ethylene polymerization with $TiCl_4/Mg(C_6H_5)_2-AlEt_2Cl$ at high temperature. Besides the facilitation of polymeric chains desorption from the catalyst surface, an easier "realkylation" of the Ti—H bond at high temperature was also hypothesized.³⁹ The desorption of bulky chains, e.g., eq. (5), followed by the regeneration of a Ti-ethyl species [eq. (4)] can result in enhancing the polymerization rate since it is known that the propagation rate is much faster for the Ti-ethyl compared to the Ti-octyl species:



Obviously, explaining the morass of reported effects requires a synthesis of all of these possible mechanisms into a coherent mechanism. This requires further experiments coupled to detail model results and will be the subject of a future paper.

Effect of Hydrogen on the Molecular Weight

The reduction of the M_n value with increasing the $[H_2]$ is strongly dependent on the catalytic system. In homogeneous catalytic systems, eq. (6) has been proposed,⁴⁰ whereas eq. (7) has been suggested to give the best fit for heterogeneous catalytic systems^{8,22}:

$$1/\bar{M}_n = a + b[H_2] \quad (6)$$

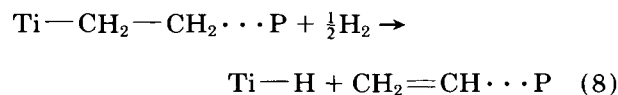
$$1/\bar{M}_n = a + b[H_2]^n \quad (7)$$

Grievson¹⁴ reported first-order dependence of lowering viscosity average molecular weight, M_n , on the H_2 pressure in the case of ethylene polymerization. However, many reports indicated that the dependence can be expressed by that of 0.5 order in propylene polymerization with $TiCl_3/AlEt_3$ ^{8,41} and in the ethylene polymerization with $TiCl_3/AlEt_2Cl$.¹³ Keii³⁴ observed that the dependence of M_n on $[H_2]$

was completely expressed by $[H_2]^{0.5}$ [eq. (7)], indicating that chain transfer by adsorbed hydrogen atoms is preferred. Guastalla and Giannini,¹⁷ using a $TiCl_4/MgCl_2-AlEt_3$ catalyst system for propylene polymerization, found that $n = 0.5$ for the molecular weight of heptane-insoluble polymer fractions. A similar observation was also observed by Böhm¹⁸ using a high-activity Ti/Mg(OH)₂-supported catalyst in ethylene polymerization.

To verify the dependence of M_n on H_2 for the solution copolymerization of ethylene, Figure 10(a) and (b) shows plots of $1/M_n$ vs. either $[H_2]$ or $[H_2]^{0.5}$. It can be observed that the plot vs. $[H_2]^{0.5}$ gives a better fit. To confirm this, curve fitting of the data using eq. (7) yields an exponent (n) equal to 0.58 [Fig. 10(c)].

Thus, the data obtained in the present investigation on the solution copolymerization of ethylene indicate that atomic hydrogen, rather than molecular hydrogen, is preferred in the chain transfer reaction, i.e., the reaction as in eq. (8) is dominant in comparison to the reaction described in eq. (2):



If this is the case, then with increasing $[H_2]$, the amount of terminal double bonds should also increase. Indeed, the results on the vinyl unsaturation indicate about 50% increase in vinyl terminal bond formation with increasing the $[H_2]$ (vinyl = 0.47 without H_2 and 0.70 at the highest H_2/C_2 ratio used). In addition, in the same range of $[H_2]$ used, M_n is also found to decrease by about 50%.

CONCLUSIONS

Ethylene copolymerization in solution has been shown to yield very high rates of polymerization. The rate-time profiles are characterized by a remarkable fast and high initial rise and very rapid decay within the 10 min polymerization time. The high maximum in R_p and the fast decay are the result of employing a high activity Ti-supported catalyst and a high polymerization temperature. The severe reactor conditions, e.g., temperature and solution viscosity, are believed to contribute to the fast decay in catalyst activity.

The increased activity in the presence of moderate H_2 concentration is believed to be due to several factors: At the very beginning of the polymerization, it seems that H_2 is creating new sites or activating

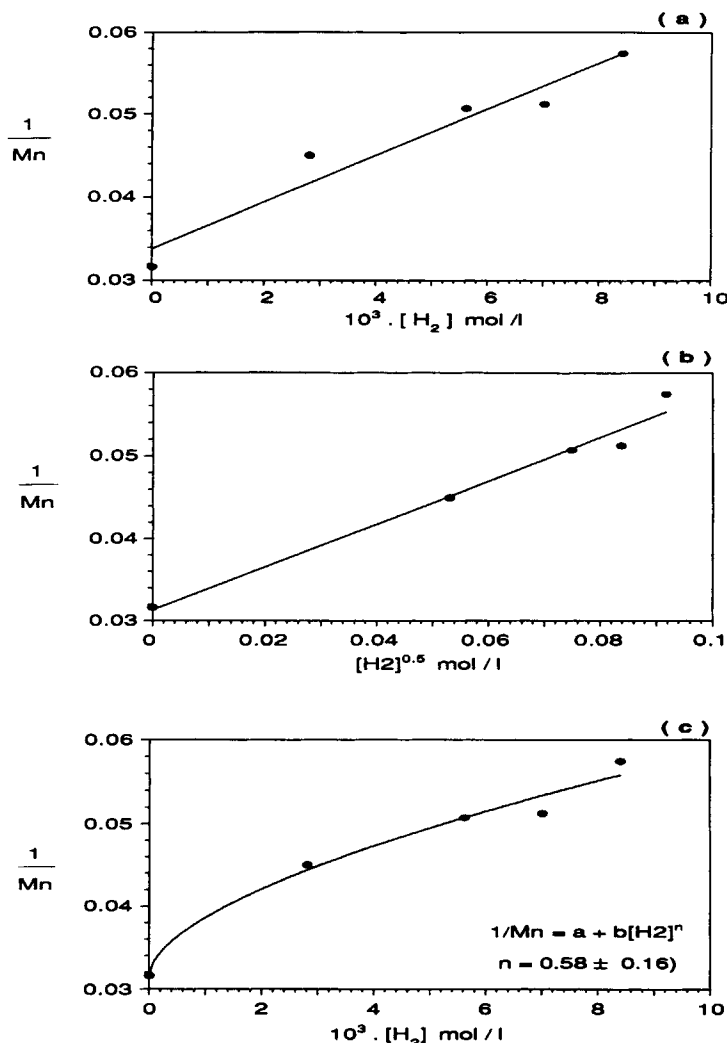


Figure 10 Plots of (a) $1/M_n$ vs. $[H_2]$, (b) $1/M_n$ vs. $[H_2]^{0.5}$, or (c) curve-fitting using the equation $1/M_n = a + b[H_2]^n$.

the dormant ones. However, these sites are highly unstable and deactivate rather fast in the first couple of minutes of polymerization. Higher activity can also result from the desorption of bulky polymeric chains, followed by the transformation of Ti—H bonds into Ti—ethyl species, which is believed to be feasible at the reactor temperature and pressure employed. Decreasing the solution viscosity is also expected to lead to higher activity by easing the mass transfer of ethylene. However, when excess hydrogen is used, the Ti—H species will be present in a large excess, thus reducing the catalyst and ultimately leading to a deactivation process.

Further results showing the effects of comonomer, solvent, temperature, and reactor pressure will be presented in subsequent papers of this series.

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