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Effect of hydrogen and of catalyst prepolymerization with propylene on the polymerization kinetics of ethylene with a non-supported heterogeneous Ziegler–Natta catalyst

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The effect of hydrogen on the polymerization rate of ethylene catalysed with a non-supported, heterogeneous Ziegler–Natta catalyst, is compared to the previously reported rate enhancement effect of hydrogen on the polymerization of propylene with the same catalyst system. It is shown that while hydrogen apparently activates new catalytic site types for the polymerization of propylene, the effect of hydrogen on the polymerization rate of ethylene is practically negligible. Prepolymerizing the catalyst with propylene increases the polymerization rate of ethylene as compared with the rate of ethylene polymerization with non-prepolymerized catalyst, but the effect of hydrogen on the polymerization rate of ethylene with the prepolymerized catalyst remains negligible. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymerization kinetics; polymerization catalysis; polyolefin characterization)

INTRODUCTION

Polyolefins are among the most important modern commodity polymers. Polyethylene and polypropylene are today the major tonnage plastic materials worldwide, accounting for 44% of all U.S. plastic sales in 1988 and reaching a capacity of about 45 million tons worldwide in 1990[1,2].

Polyolefins are commercially-produced using free-radical initiators, Phillips type catalysts, and Ziegler–Natta catalysts. Of these processes, those based on Ziegler–Natta catalysts are the most important because of their very broad range of applications.

Although there are many different types of heterogeneous Ziegler–Natta catalysts, most of them have a common intriguing characteristic: they yield polymer with broad molecular weight distribution (MWD) and, in the case of copolymerization, broad chemical composition distribution (CCD). There is now a general agreement that heterogeneous Ziegler–Natta catalysts possess more than one type of active site, each with distinct ratios of chain transfer to propagation rates, comonomer reactivity ratios, and stereoselectivites. Since polymer chains made by each site type have different average chain lengths, different comonomer compositions, different comonomer sequence lengths and, in the case of asymmetric monomers, different degrees of stereoregularity, the bulk polymer made with heterogeneous Ziegler–Natta catalysts is in reality a mixture, at the molecular level, of polymer chains having dissimilar average properties. These dissimilar average properties are reflected in the broad MWDs and CCDs that are frequently observed in polymers made with heterogeneous Ziegler–Natta catalysts. Additionally, intraparticle heat and mass transfer resistances during the polymerization may broaden these distributions even further[3].

On the other hand, polyolefins made with most soluble Ziegler–Natta catalysts have narrow MWD, and copolymers also have narrow CCD. This behaviour supports the multiple-site type hypothesis for heterogeneous catalysts. Soluble Ziegler–Natta catalysts consist of reasonably well defined, single catalytic species, probably not subject to heat and mass transfer resistances during polymerization.

It is useful to interpret the broad MWD and CCD of polymers obtained with Ziegler–Natta catalysts as resulting from the superposition of individual MWDs and CCDs of polymer chains produced on each type of active site[4,5].

It is generally accepted that, under most polymerization conditions, the effect of multiple site types is far

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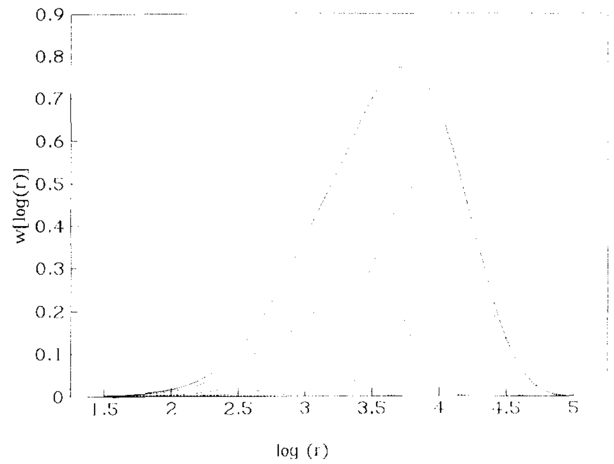

Figure 1 Instantaneous MWD of a polyolefin made with a multiple site type catalyst as a superposition of four individual Flory's most probable MWDs. (Solid line indicates MWD of accumulated polymer and dotted lines represent MWDs of polymer made on distinct active sites)

more important than mass and heat transfer resistances. Under these conditions, each site type instantaneously produces polymer that is assumed to have Flory's most probable MWD[6]. Therefore, the instantaneous MWD of accumulated polymer made with heterogeneous Ziegler–Natta catalysts can be considered an average of that produced by the individual site types, weighted by the weight fraction of polymer produced by each site type (*Figure 1*).

The objective of this work is to compare the effect of hydrogen on the polymerization rate of ethylene with the data reported by Soares and Hamielec[7] for propylene polymerization using the same catalytic system.

EXPERIMENTAL

A semi-batch slurry reactor was used to study the kinetics of ethylene polymerization with a titanium trichloride heterogeneous Ziegler–Natta catalyst. The MWD of polyethylene produced during this stage was further analysed with s.e.c..

Polymerization runs

All polymerizations were carried out in a 1-l stainless steel autoclave reactor operated in semi-batch mode. Purified diluent (500 ml) was transferred to the reactor under nitrogen pressure through a transfer needle. Cocatalyst solution and catalyst slurry were injected in the reactor using gas-tight syringes. In all experimental runs, the order of injection was cocatalyst solution first, followed by the catalyst slurry. The interval between injections never exceeded 10 min. If necessary, the reactor was initially pressurized with hydrogen to act as a chain transfer agent. Unless otherwise stated, hydrogen was not fed to the reactor at any other time during the polymerization. The polymerization was started by feeding gaseous ethylene as required to maintain a constant pressure in the reactor. The flow rate of ethylene fed to the reactor was measured with an on-line mass flow meter, as shown in *Figure 2*. The polymerization was interrupted by rapid depressurization of the head space of the reactor followed by quenching of the catalyst with methanol. *Figure 2* illustrates the polymerization reaction system.

The catalyst used was LYNX 900, a second generation, ester modified titanium trichloride catalyst, kindly donated by CRI, Catalyst Resources, Inc. The cocatalyst used was diethyl aluminium chloride (DEAC) from Aldrich. The diluent, isoparaffin 2025 from Shell

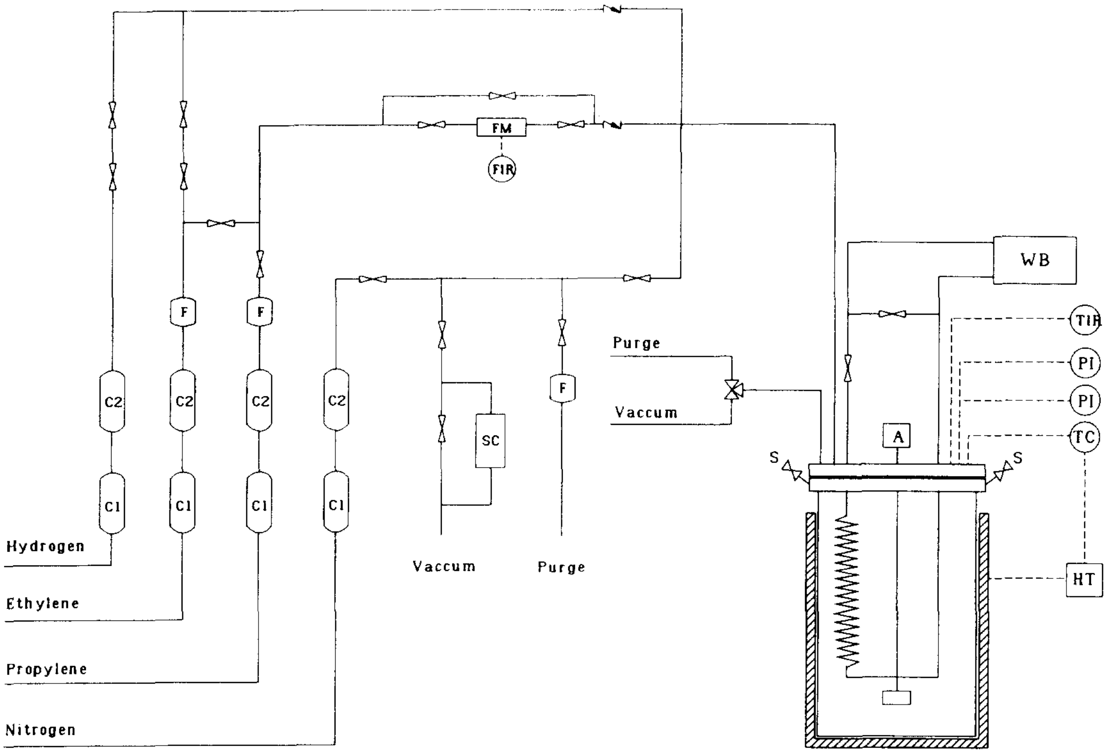

Figure 2 Polymerization reactor system: A, stirrer; S, septum inlet; WB, thermostated water bath; HT, heater; TC, temperature controller; PI, pressure indicator; TIR, temperature indicator and recorder; C1, oxygen trap column; C2, dehumidifier column; F, on-line filter; FM, mass flow meter; FIR, flow indicator and recorder; SC, solvent condenser

Table 1 Experimental conditions and yield of ethylene polymerization runs

Run #	Prep	T	P_{ethylene}	P_{H2}	[TiCl$_3$]	[DEAC]	[DEAC]/[TIC$_3$]	Catalyst activity
HE004	N	60	70	0	1.83	8.29	4.53	657.0
HE006	N	60	70	0	1.78	8.00	4.50	522.5
HE005	N	60	70	10	1.79	8.14	4.54	549.2
HE007	N	60	70	10	1.78	8.01	4.50	602.4
HE013	Y	50	70	0	1.77	7.91	4.47	2117.4
HE021	Y	50	70	0	1.75	8.16	4.65	1779.5
HE012	Y	50	70	10	1.79	7.92	4.41	1583.6
HE022	Y	50	70	10	1.77	7.93	4.47	1534.7
HE009	Y	60	70	0	1.73	8.09	4.69	2713.1
HE016	Y	60	70	0	1.76	8.11	4.61	3055.7
HE014	Y	60	70	5	1.74	7.94	4.55	2978.8
HE008	Y	60	70	10	1.73	8.02	4.64	2703.6
HE015	Y	60	70	10	1.77	8.13	4.60	2956.7
HE011	Y	70	70	0	1.79	7.92	4.41	4833.2
HE019	Y	70	70	0	1.75	8.13	4.64	4084.6
HE010	Y	70	70	10	1.78	8.17	4.60	3918.2
HE020	Y	70	70	10	1.81	8.01	4.43	3274.7

Prep: Y, catalyst prepolymerized with propylene, N, regular catalyst; T, polymerization temperature, °C; P_{ethylene}, partial pressure of ethylene, psi; P_{H2}, partial pressure of hydrogen, psi; [TiCl$_3$], catalyst concentration, mmol l^{-1}; [DEAC], cocatalyst concentration, mmol^{-1}; Catalyst activity, g polymer g $\mathrm{catalyst}^{-1}$ mol^{-1} h^{-1}

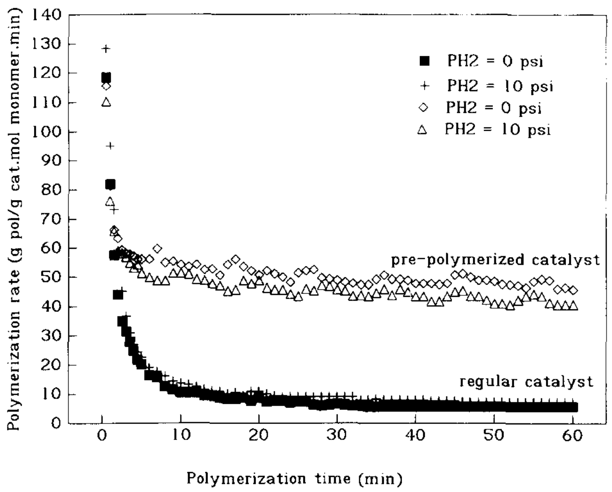

Figure 3 Effect of catalyst prepolymerization with propylene on the polymerization rate of ethylene at 60°C (polymerization rate calculated using total moles of ethylene absorbed in the diluent)

Canada, was purified over molecular sieves under nitrogen pressure.

When necessary, the catalyst was prepolymerized with propylene by pressurizing the reactor containing diluent, catalyst slurry and cocatalyst solution with a propylene partial pressure of 12 psi for 5 min. All effort was taken to minimize copolymerization effects that could occur if significant amounts of propylene stayed in the reactor after the prepolymerization. The prepolymerization was terminated by evacuating and venting the reactor with nitrogen exhaustively to assure the proper removal of the propylene absorbed in the diluent. The polymerization of ethylene was started immediately after propylene removal.

Research grade ethylene (99.99%) cylinders were purchased from Matheson. Ultra high purity nitrogen (99.999%) and ultra high purity hydrogen (99.999%) cylinders were purchased from Canadian Liquid Air/ Alphagaz. Further purification of gaseous streams was provided by on-line oxygen traps and dessicator columns (*Figure 2*). All gas cylinders were provided with two-stage regulators to ensure precise pressure control during polymerization.

A detailed description of the polymerization procedure is given by Soares[8].

Polymer characterization

MWDs of the polyethylene samples were measured with a Waters-Millipore s.e.c. instrument model 150-C. The following operation conditions were adopted: 1) column and sample compartment temperature, 145°C; 2) flow rate of mobile phase, 1.0 ml min^{-1}; 3) sample injection volume, 200 μl; 4) no sample spinning; 5) no sample filtering; 6) sample concentration, 0.1 wt% in trichlorobenzene. Antioxidant (Irganox 1010 from Ciba-Geigy) was also added to the sample vials at a concentration of 0.1 wt% to prevent oxidative thermal degradation of polyethylene in the s.e.c. oven and columns. No antioxidant was added to the mobile phase. MWDs and averages were determined using the universal calibration curve obtained with narrow MWD polystyrene standards.

RESULTS

Polymerization rate

Ethylene was polymerized at three different temperatures and three different hydrogen pressures. The effect of prepolymerization was also investigated. Monomer partial pressure, catalyst, and cocatalyst concentrations were kept constant for all runs. *Table 1* shows the experimental design adopted for the polymerizations, the reactor operation conditions, and polymer yields of each run.

Table 2 Effect of prepolymerization with propylene in catalyst activity of ethylene polymerization

	Regular catalyst		Prepolymerized catalyst	
T	Catalyst activity	Standard deviation	Catalyst activity	Standard deviation
50			1753.8	264.5
60	582.8	59.6	2881.6	162.4
70			4027.7	640.6

T, polymerization temperature, °C; catalyst activity, g polymer g catalyst^{-1} mol^{-1} h^{-1}

Table 3 Statistical significance of the influence of hydrogen on the polymerization rate of ethylene

Prep	*T*	t_0	ν	Pr
N	60	0.19	2	>0.4
Y	50	2.28	2	0.08
Y	60	0.027	3	>0.4
Y	70	1.75	2	0.12

Prep: Y, catalyst prepolymerized with propylene, N, regular catalyst; *T*, polymerization temperature, °C; t_0, normalized deviate; Pr, level of probability; ν, degrees of freedom

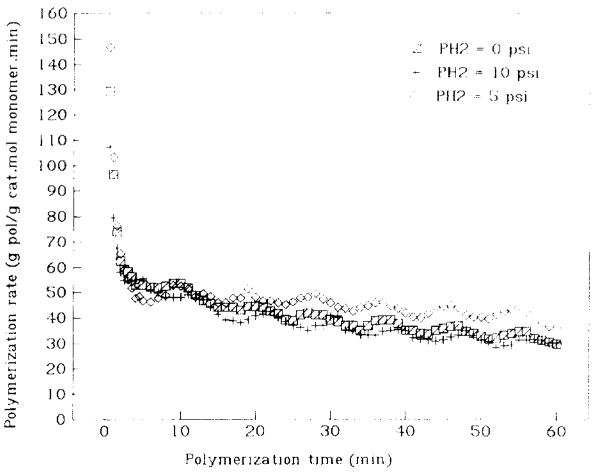

Figure 4 Effect of hydrogen pressure on polymerization rate of ethylene at 60°C with prepolymerized catalyst (polymerization rate calculated using the total moles of ethylene absorbed in the diluent)

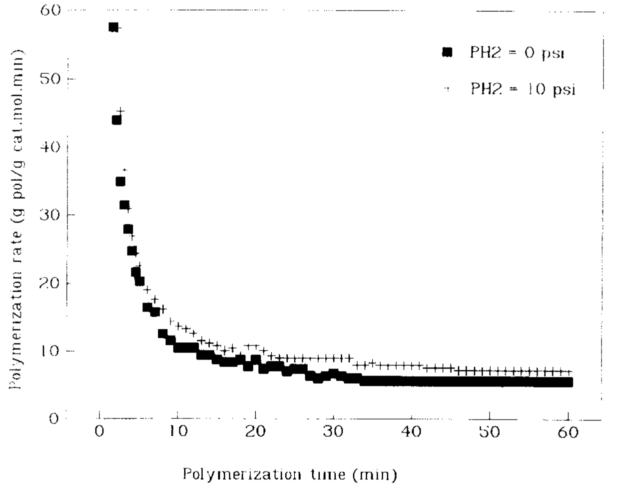

Figure 5 Effect of hydrogen pressure on polymerization rate of ethylene at 60°C with regular catalyst (polymerization rate calculated using the total moles of ethylene absorbed in the diluent)

Prepolymerization of the catalyst with propylene prior to ethylene polymerization has a remarkable effect of the activity of the catalyst towards ethylene polymerization. As shown in *Figure 3*, when the prepolymerized catalyst is used the polymerization rate of ethylene increases significantly when compared to the polymerization rates obtained with the regular catalyst. This acceleration rate effect is observed either in the presence or in the absence of hydrogen. *Table 2* shows the average polymerization rates of the regular and prepolymerized catalyst at the three temperature levels studied. In *Figure 3*, the oscillations observed in the polymerization rate of ethylene were caused by the reactor pressure controller and should not be considered as actual oscillations of the polymerization rate. The same remark is valid for *Figure 4*.

The effect of hydrogen on the polymerization rate of ethylene is not so clear as is the effect of hydrogen on the polymerization rate of propylene[7]. By inspection of *Table 1* for the case of the regular catalyst, there seems to be no significant influence of hydrogen on the polymerization rate of ethylene. On the other hand, for the prepolymerized catalyst, the presence of hydrogen apparently decreases the catalyst activity slightly, especially at 50 and 70°C. However, these observed differences are not statistically significant. *Table 3* shows the levels of probability of the null hypothesis for the influence of hydrogen in the polymerization rate of ethylene in relation to the Student's distribution[9]. The null hypothesis states that the average polymerization rate of ethylene in absence of hydrogen is equal to the average polymerization rate of ethylene in presence of hydrogen. The null hypothesis is clearly valid for both the regular and the prepolymerized catalyst at 60°C. At 70°C, the difference in the average rate of polymerization is statistically significant at the 0.12 level of probability, which is still sufficiently high to support the null hypothesis. However, at 50°C the difference in rates of polymerization is statistically significant at the smaller level of probability of 0.08. At this level of probability it is somewhat difficult to make a decisive distinction between accepting or rejecting the null hypothesis. However, since the polymerization rate of ethylene is clearly not considerably affected by the presence of hydrogen at 60°C and likely not at 70°C, it seems reasonable to assume that hydrogen will not significantly influence the rate of ethylene polymerization at 50°C.

Figure 4 shows the polymerization kinetic curves of ethylene at 60°C in the absence of hydrogen and at hydrogen partial pressures of 5 and 10 psi for the prepolymerized catalyst. The initial decrease in ethylene flow actually corresponds to the pressurization of the polymerization reactor and should not be interpreted as decay in catalytic activity. *Figure 5* shows the polymerization kinetic curves of ethylene at 60°C in the absence of hydrogen and at hydrogen partial pressure of 10 psi for the regular catalyst. No significant hydrogen effects on the rate of polymerization were observed in either case.

Table 4 shows the average rates of polymerization and

Table 4 Effect of hydrogen on catalyst activity of ethylene polymerization

		$P_{H_2} = 0$		$P_{H_2} \neq 0$	
T	Prep	Catalyst activity	Standard deviation	Catalyst activity	Standard deviation
60	N	589.8	95.1	575.8	37.6
50	Y	1948.5	238.9	1559.2	34.6
60	Y	2884.4	242.3	2879.7	152.9
70	Y	4458.9	529.3	3596.5	455.0

T, temperature, °C; Prep: Y, catalyst prepolymerized with propylene, N, regular catalyst; P_{H2}, partial pressure of hydrogen, psi; catalyst activity, g polymer g catalyst^{-1} mol^{-1} h^{-1}

Table 5 Molecular weight averages and polydispersities of polyethylene (measured by high temperature s.e.c.)

Pre-polym	P_{H_2} (psi)	T (°C)	M_n	M_w	PDI
Yes	10	60	112400	330000	2.94
No	10	60	97700	311200	3.18
Yes	0	60	188300	440900	2.34
No	0	60	178500	416800	2.34

standard deviations at each polymerization temperature in presence and absence of hydrogen.

The activation energy of polymerization defined by the Arrhenius law is expressed as:

$$Y = k_p C^* [M] \quad (1)$$

$$Y = k_{p0} \exp(-E/RT) C^* [M] \quad (2)$$

$$\ln Y/[M] = -E/RT + \ln k_{p0} C^* \quad (3)$$

where Y is the polymer yield rate of polymerization, in mol h^{-1}; k_p is the average propagation kinetic constant, in l mol^{-1} h^{-1}; C^* is the number of active sites, in mol; [M] is the ethylene concentration, in mol l^{-1}; k_{p0} is the pre-exponential factor, in l mol^{-1} h^{-1}; E is activation energy, in kcal mol^{-1}; R is the gas constant, in kcal mol^{-1} K^{-1}; and T is temperature, in K.

The activation energy E, estimated from the slope of the curve ln Y/[M] *versus* $1/T$, is equal to 11 300 cal mol^{-1} for ethylene polymerization with the prepolymerized catalyst. The value is in the range commonly reported in the literature for activation energy of ethylene polymerization[10].

Polymer characterization

Soares and Hamielec[7] reported a significant hydrogen rate enhancement effect for the polymerization of propylene with this catalytic system, with consequent broadening of molecular weight distribution and stereoregularity distribution. On the other hand, for the case of ethylene polymerization, hydrogen does not seem to have a marked influence on catalyst activity, as attested by *Figures 4* and *5*.

However, prepolymerization with propylene before introduction of ethylene causes a marked increase in the polymerization rate of ethylene. The molecular weight averages of polyethylene samples polymerized at 60°C with or without prepolymerizaiton and in presence or absence of hydrogen are shown in *Table 5*. Prepolymerization of the catalyst with propylene increases the averaged molecular weights but does not alter polydispersity. The presence of hydrogen increases polydispersity but not as significantly as for the case of propylene polymerization. This increase in the polydispersity of polypropylene obtained in the presence of hydrogen can be related to the activation of new site types on the catalyst[7].

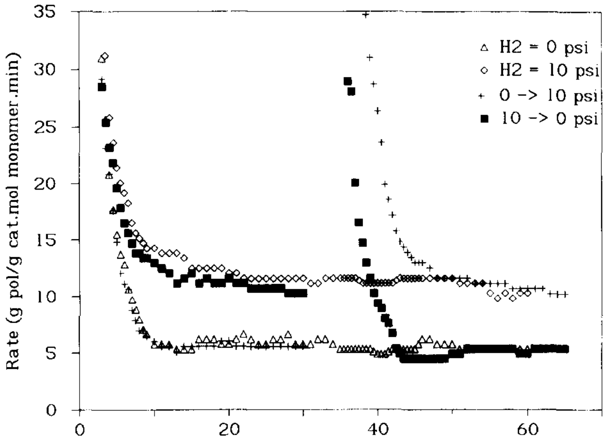

Figure 6 Reversibility of hydrogen effect on polymerization rate of propylene at 70°C (polymerization rate calculated using the total moles of propylene absorbed in the diluent)

DISCUSSION

The effect of hydrogen on the rate of olefin polymerization with Ziegler–Natta catalysts is rather complex and governed by insufficiently known mechanisms[11,12]. Depending on the type of catalyst, cocatalyst, monomer, and polymerization conditions, the polymerization rate can either decrease[13–18], increase[7,18–24], or remain unaffected[18,25,26] in the presence of hydrogen.

More interesting to our experimental results, we[7] studied the effects of hydrogen on the polymerization of propylene using the same catalytic system as the present study, through an integrated methodology of polymer kinetics determination and polymer characterization via s.e.c./TREF/^{13}C n.m.r. We found that the presence of hydrogen significantly increased the rate of propylene polymerization and broadened the MWD and stereoregularity distribution of the formed polymer. The effect of hydrogen was also shown to be reversible; removal of hydrogen from the reactor would decrease the polymerization rate to values obtained when the polymerization was started in absence of hydrogen (*Figure 6*). It was proposed that hydrogen activated catalytic sites that were dormant in its absence.

Hydrogen, however, has a minimal effect on polymerization rate of ethylene with the regular or prepolymerized catalyst as shown in *Figures 4* and *5*. Since hydrogen does have a significant rate enhancement role during propylene polymerization using this same catalytic system, it seems that the activation mechanism by hydrogen is based on an interaction between hydrogen, monomer, and catalyst, as proposed by Ross[24]. Therefore, hydrogen will not interact with ethylene to form new active sites on the catalyst, but it will interact with propylene, forming new site types with consequent increase in polymerization rate and broadening of the

MWD and stereoregularity distribution. That propylene has to be present as a monomer is evident from the results using the prepolymerized catalyst; although in this case polypropylene is present during the polymerization, no rate enhancement effect is observed due to the presence of hydrogen. This mechanism is only tentative and only with more extensive experimental data could one establish its validity. Alternatively, the hydrogen-activated sites might not be active for ethylene polymerization.

The enhancement of the rate of ethylene polymerization caused by the presence of an α-olefin has been studied in industrial and academic laboratories[27]. Two principal experimental conditions may lead to this phenomenon: 1) prepolymerization of the catalyst with an α-olefin prior to the addition of ethylene to the reactor; 2) copolymerization of ethylene and an α-olefin. The rate of propylene homopolymerization can also be increased by prepolymerization of the catalyst at milder conditions with propylene[28].

Several explanations have been proposed to account for rate enhancement by prepolymerization: 1) controlled fracturing of the catalyst during prepolymerization, exposing more active sites[29,30]; 2) activation of dormant sites or formation of additional sites by the α-olefin[31–33]; 3) displacement of complexed molecules, such as donor molecules formed during catalyst synthesis or added on purpose as external Lewis bases, by the α-olefin[32]; 4) change of the distribution of the titanium oxidation states[34]; and 5) alteration of the association state of the titanium[27]. Reduction of diffusional mass transfer resistances of the cocatalyst and monomer through the polymeric layer surrounding the active sites has also been suggested for the case of rate enhancement of copolymerization of ethylene and α-olefins[35].

It is difficult to determine which one of the above mechanisms is responsible for the increase in the polymerization rate of ethylene using the prepolymerized catalyst. Due to the complex nature of heterogeneous Ziegler–Natta catalysts, it is probable that several of those mechanisms are present simultaneously in different degrees as a function of the polymerization conditions, type of catalytic system, and type of monomer.

Based on our polymerization rate and polymer characterization data, we can tentatively propose that prepolymerization with propylene generates sites with higher propagation constants and smaller ratios of chain transfer to propagation rates than those created when the catalyst is directly contacted with ethylene, but does not necessarily produce more types of active sites. This hypothesis is supported by the higher catalytic activities and polymer with higher molecular weight averages obtained with the prepolymerized catalyst with no or little change in polydispersities.

One can envisage a polymerization process in which ethylene when put in contact directly with the catalyst, due to its very high reactivity, polymerizes very fast with incomplete breakup of the original particle or even restricting access of monomer to the active sites by encapsulating them.

On the other hand, prepolymerizing the catalyst with the less reactive propylene might lead to a more controlled breakup of the particles and the formation of a catalyst–polymer particle of high porosity where ethylene can be polymerized with higher activities.

CONCLUSIONS

Hydrogen has a negligible effect in the polymerization rate of ethylene using regular or prepolymerized LYNX 900/DEAC catalyst. Since hydrogen significantly enhances the rate of propylene polymerization using the same catalytic system, it seems that the combined interaction of hydrogen, monomer, and catalyst is required for the formation of new active site types on the catalyst.

The activity of this catalyst towards ethylene polymerization can be significantly increased by prepolymerization with propylene. It is possible that the more controlled breakup of the catalyst particles with propylene, exposing more active sites to polymerization, is partially responsible for this behaviour.

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