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Kinetics of propylene polymerization with a non-supported heterogeneous Ziegler–Natta catalyst—effect of hydrogen on rate of polymerization, stereoregularity, and molecular weight distribution

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The effect of hydrogen on the kinetics of polymerization of propylene catalysed with a non-supported, heterogeneous Ziegler–Natta catalyst, was studied using an integrated measurement methodology of polymerization rate determination and polymer characterization using size exclusion chromatography, temperature rising elution fractionation, and ^{13}C nuclear magnetic resonance. It was unequivocally shown that the presence of hydrogen during the polymerization of propylene activates catalytic sites that are dormant when hydrogen is absent, increasing the polymerization rate and broadening the distributions of molecular weight and stereoregularity. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymerization kinetics; Ziegler–Natta catalysis; temperature rising elution fractionation)

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 US plastic sales in 1988, and reaching a capacity of about 45 million tons in 1990[1,2].

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

Ziegler–Natta catalysts have evolved considerably since their discovery by Ziegler and Natta in the early fifties until today, with the development of new catalyst generations and industrial processes. This class of catalysts has been used in homogeneous, heterogeneous and colloidal forms to synthesize high-density polyethylene, isotactic polypropylene, ethylene–propylene copolymers, *cis*-1,4-polybutadiene, and *cis*-1,4-polyisoprene among other products. Recently, the discovery of a new class of soluble Ziegler–Natta catalyst, metallocenes with aluminoxane and other cocatalysts, seems to have opened the door to a new revolution in the production of polyolefins. Metallocene catalysts with appropriate cocatalysts are able to produce polyolefins at a very high productivity, with a degree of microstructural control not possible using conventional Ziegler–Natta catalysts.

Although there are many different types of heterogeneous Ziegler-Natta catalysts, most 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 general agreement that heterogeneous Ziegler–Natta catalysts possess more than one type of active site, each one with distinct ratios of chain transfer to propagation rates, comonomer reactivity ratios, and stereoselectivities. Since polymer chains made by each site type have different average chain lengths, comonomer compositions, comonomer sequence lengths and, in the case of asymmetric monomers, different degrees of stereoregularity, the whole polymer made with heterogeneous Ziegler–Natta catalysts is in reality a mixture, at the molecular level, of polymer chains having very 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 MWDs, and

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copolymers also have narrow CCDs. 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.

The complexity of MWDs and CCDs of polyolefins made with Ziegler–Natta catalysts constitutes a challenging problem for polymer quality control. Most properties of polyolefins are routinely measured only as average values. Measurements of melt flow index (as an estimator for molecular weight averages), melt flow index ratio (as an estimator of polydispersity), and moulded density (as an estimator of copolymer composition or degree of short chain branching) are common practice in industry. However, it is important to recall that the macroscopic properties of polymers in general, and polyolefins in particular, cannot be uniquely determined by average values, since polymers that have some average properties in common can possess other properties that differ markedly. Even a knowledge of the full molecular weight distribution for polypropylene may not be sufficient for many practical applications, due to stereoirregularities. In the same way, determining average compositions of copolymers or average degrees of branching will not entirely define the polymer in question. The whole distribution of composition in addition to chain length is necessary to accomplish this task. This issue becomes even more complex with polyolefins made with Ziegler–Natta catalysts, because polymers with broad and sometimes multimodal MWDs and CCDs are often produced.

The concern about the breadth of MWD and CCD of polyolefins is far from academic. Those distributions affect the final mechanical and rheological properties of polyolefins, and ultimately determine their applications. Polyethylenes with broad MWDs are easier to process, because of greater flowability in the molten state at high shear rate, while polyethylenes with narrow MWDs have greater dimensional stability, higher impact resistance, greater toughness at low temperatures, and higher resistance to environmental stress cracking. For polypropylene, a narrow MWD is required for rapid moulding of products with good mechanical properties.

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 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 study the effect of hydrogen on the polymerization of propylene with a heterogeneous Ziegler–Natta catalyst using an integrated measurement methodology of polymerization rate determination and polymer characterization with high temperature size exclusion chromatography (s.e.c.), temperature rising elution fractionation (TREF), and ^{13}C nuclear magnetic resonance spectroscopy (^{13}C n.m.r.).

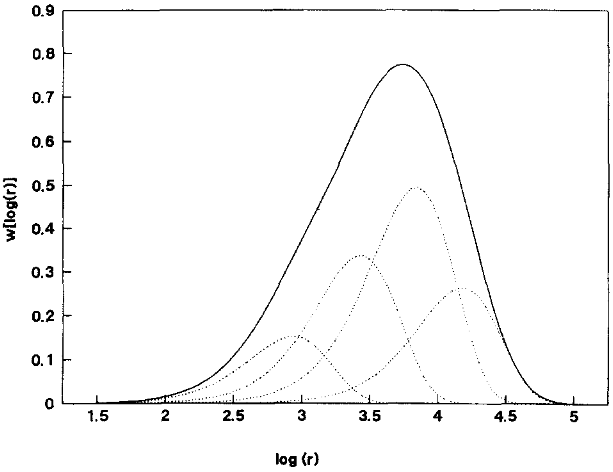

Figure 1 Instantaneous MWD of a polyolefin made with a multiple site type catalyst as a superposition of four individual Flory's most probable MWDs. (Solid line indicates MWD of the whole polymer and dotted lines represent MWDs of polymers made on distinct active site types)

EXPERIMENTAL

A semi-batch slurry reactor was used to study the kinetics of propylene polymerization with a titanium trichloride heterogeneous Ziegler-Natta catalyst. The microstructure of polymer produced was further characterized using s.e.c., TREF, and ^{13}C n.m.r.

Polymerization runs

All polymerizations were carried out in a 1-l stainless steel autoclave reactor operated in semi-batch mode. Purified diluent 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 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 monomer on demand to maintain a constant pressure in the reactor. The flow rate of propylene fed to the reactor was measured with an on-line mass flow meter. 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 Canada, was purified over molecular sieves under nitrogen pressure.

Polymerization grade propylene (99.5%) cylinders were purchased from Matheson. Ultra high purity

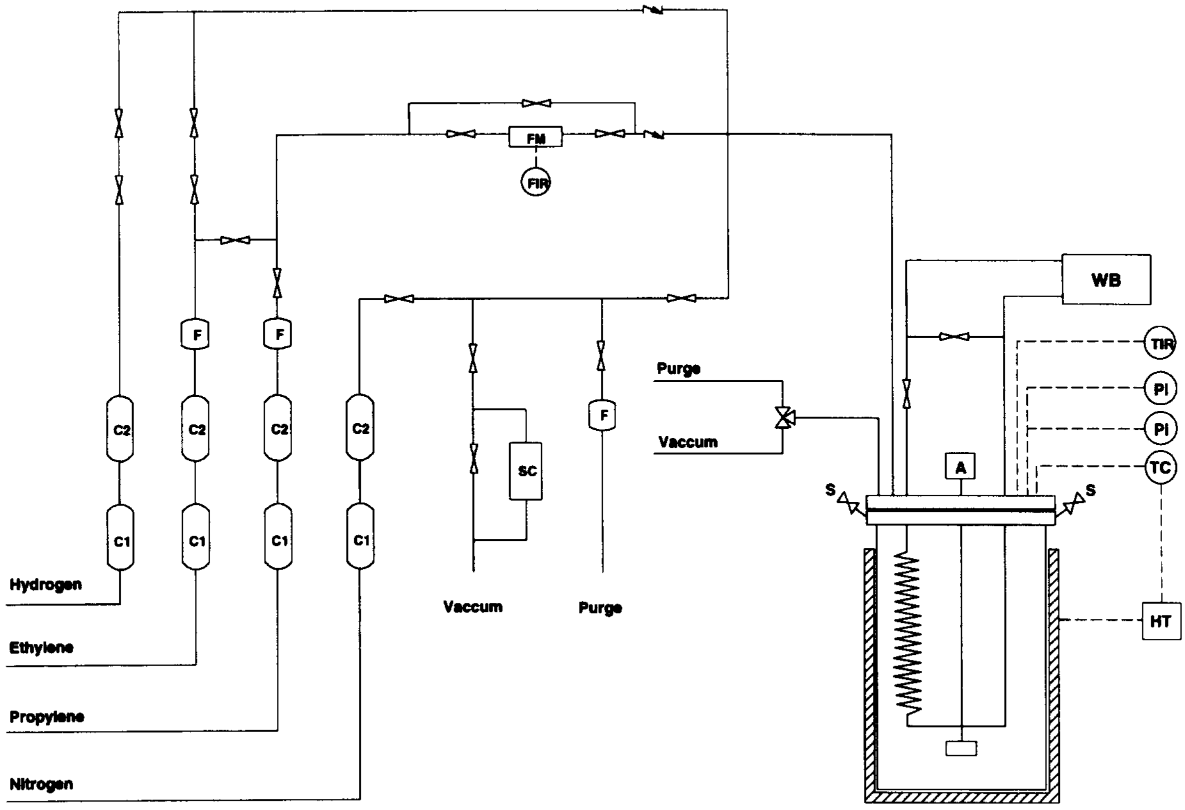

Figure 2 Polymerization reactor system. A, stirrer; S, septum inlet; WB, thermostated water bath; HT, heater; TC, temperature controller; PI, pressure indicator; TIR, temperature indicator and recorder; C1, oxygen trap column; C2, dehumidifier column; F, in-line filter; FM, mass flow meter; FIR, flow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

Table 1 Experimental conditions and yield of propylene polymerization runs

Run #	T	P_{propene}	P_{H2}	[TiCl$_3$]	[DEAC]	[DEAC]/[TICl$_3$]	Catalyst activity
HP057	50	70	0	1.76	7.98	4.53	164.7
HP058	50	70	0	1.76	8.02	4.56	148.5
HP056	50	70	10	1.74	8.02	4.61	245.6
HP059	50	70	10	1.76	8.00	4.55	259.8
HP054	60	70	0	1.56	8.02	5.14	230.0
HP052	60	70	0	1.74	8.00	4.60	262.9
HP053	60	70	5	1.72	7.92	4.60	418.4
HP051	60	70	10	1.74	8.00	4.60	432.0
HP055	60	70	10	1.76	8.02	4.56	493.7
HP045	70	70	0	1.76	8.10	4.60	382.7
HP046	70	70	0	1.76	7.14	4.06	408.8
HP050	70	70	2	1.76	8.02	4.56	716.1
HP041	70	70	5	1.78	8.12	4.56	748.7
HP042	70	70	5	1.76	8.00	4.55	768.8
HP043	70	70	10	1.80	8.08	4.49	765.9
HP044	70	70	10	1.76	8.06	4.58	733.5

T, polymerization temperature, °C; P_{propene}, partial pressure of propene, psi; P_{H2}, partial pressure of hydrogen, psi; [TiCl$_3$], catalyst concentration, mmol l^{-1}; [DEAC], cocatalyst concentration, mmol l^{-1}; catalyst activity, g polymer g catalyst^{-1} mol^{-1}

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 in-line oxygen traps and dessicator columns (*Figure 2*). All gas cylinders were provided with two-stage regulators to ensure precise pressure control during polymerization.

Polymer characterization

MWDs of the polyolefin 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 polypropylene 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.

All TREF runs were performed in the fractionation apparatus described by Soares and Hamielec[7]. The samples that will be the subject of discussion in the next section were all fractionated by using TREF in preparative mode.

Detailed structural information about the polymer chains was obtained by analysing the ^{13}C n.m.r. spectra of the fractions using standard n.m.r. techniques for polyolefins[8].

A detailed description of the polymerization procedure and characterization techniques is given by Soares[9].

RESULTS

Polymerization rate

Propylene was polymerized at three different temperatures and four different hydrogen pressures. Monomer partial pressure, catalyst and cocatalyst concentrations were the same for all runs. *Table 1* summarizes the experimental design adopted and shows reactor operation conditions and polymer yields of each run.

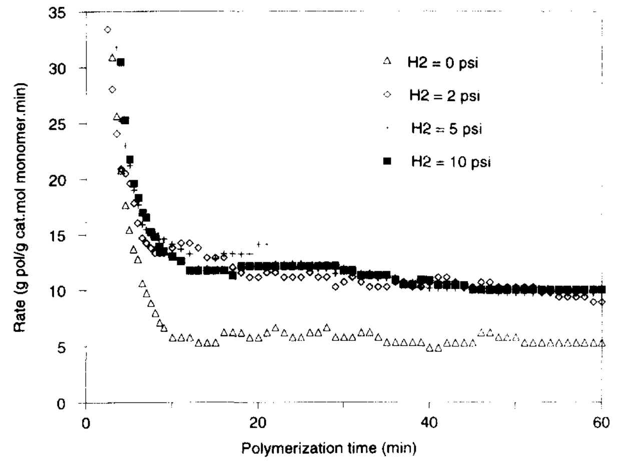

Figure 3 Effect of hydrogen pressure on polymerization rate of propylene at 70°C

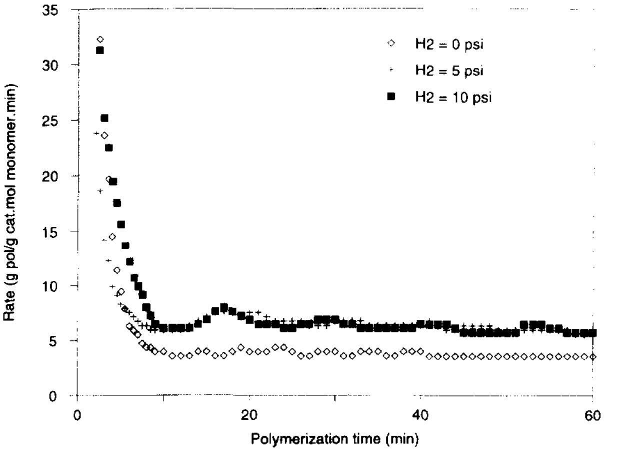

Figure 4 Effect of hydrogen pressure on polymerization rate of propylene at 60°C

The presence of hydrogen in the reactor significantly increased the catalyst activity for all three temperature levels studied. *Figure 3* shows the polymerization rate curves of propylene at 70°C in absence of hydrogen and at hydrogen partial pressures of 2, 5, and 10 psi. The initial decrease in propylene flow rate actually corresponds to the pressurization of the polymerization reactor and should not be considered as a catalytic decay period. The catalyst activity is significantly increased by initially pressurizing the reactor with even small pressures of hydrogen. Increasing hydrogen pressure from 2 to 10 psi does not seem to increase catalyst activity any further. The same behaviour was noticed at polymerization temperatures of 60°C and 50°C as shown in *Figures 4* and *5*. *Table 2* shows the average rates of polymerization and standard deviations at each polymerization temperature in presence and absence of hydrogen (all polymerizations were replicated twice).

In order to test the reversibility of the hydrogen effect on polymerization rate, two additional experiments were designed for the polymerization temperature of 70°C. In the first one, the polymerization of propylene was initiated with a hydrogen partial pressure of 10 psi. After 30 min the polymerization was shortly interrupted by stopping the monomer flow and depressurizing the reactor. The reactor was then connected to the vacuum line for 5 min to eliminate residual amounts of hydrogen dissolved in the diluent. The polymerization was restarted by pressurizing the reactor with propylene, this time

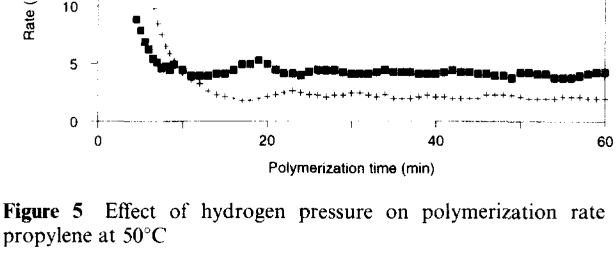

Figure 5 Effect of hydrogen pressure on polymerization rate of propylene at 50°C

Table 2 Effect of hydrogen on catalyst activity of propylene polymerization

	$P_{H_2} = 0$		$P_{H_2} \neq 0$	
T	Catalyst activity	Standard deviation	Catalyst activity	Standard deviation
50	156.6	11.5	252.7	10.0
60	246.5	23.3	448.0	40.1
70	395.8	18.5	746.6	22.2

P_{H2}, partial pressure of hydrogen; T, temperature, °C; catalyst activity, g polymer g catalyst^{-1} mol^{-1} h^{-1}

in absence of hydrogen. This second stage of polymerization was interrupted after 30 min by quenching with methanol. In the second experiment, the reverse order was adopted. The polymerization was started in absence of hydrogen and after 30 min of polymerization the reactor was pressurized with 10 psi of hydrogen, after which the polymerization continued for an additional 30 min.

Figure 6 compares the two experiments described in the last paragraph with a polymerization in absence of hydrogen and another in which an initial partial pressure of hydrogen was used. The agreement between the curves is quite remarkable, leading to the conclusion that the effect of hydrogen on the activity of the catalyst for propylene polymerization is reversible. Admission of hydrogen to a polymerization started in the absence of hydrogen immediately causes the rate of polymerization to increase to the level observed when the polymerization was started in the presence of hydrogen. In the same way, when hydrogen is evacuated from the reactor, the polymerization rate drops to the value obtained when no hydrogen is used throughout the polymerization.

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

$$Y = k_p[C^*][M] \tag{1}$$

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

$$\ln\frac{Y}{[M]} = -\frac{E}{RT} + \ln k_{p0}[C^*] \tag{3}$$

where Y is the polymer yield rate, k_p is the average propagation kinetic constant, $[C^*]$ is the concentration of active sites, $[M]$ is monomer concentration, k_{p0} is a pre-exponential factor, E is the activation energy, R is the gas constant, and T is temperature.

The activation energy E can be thus estimated from the slope of the curve $\ln Y/[M]$ *versus* $1/T$.

The estimated activation energy for propylene polymerization in the presence of hydrogen was 15 600 cal mol^{-1}, and for propylene polymerization in the absence of hydrogen, 13 800 cal mol^{-1}. Those values are in the range commonly reported in the literature for the activation energy of propylene polymerization[10].

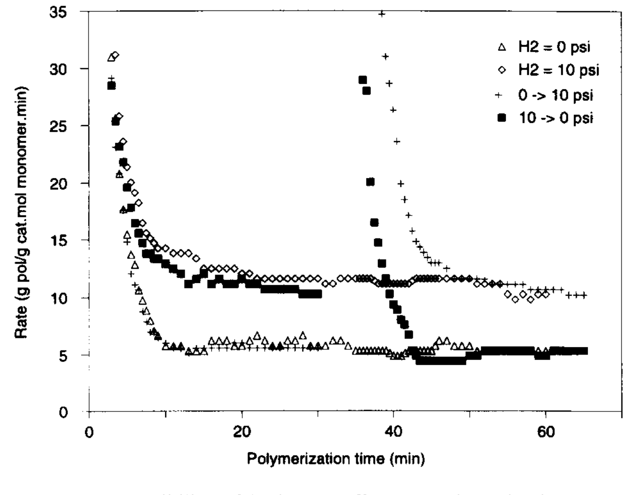

Figure 6 Reversibility of hydrogen effect on polymerization rate of propylene at 70°C

Polymer characterization

The MWDs of polypropylene were determined by SEC following the procedures described above.

Table 3 shows the results for the number and mass average molecular weights and polydispersity of the polypropylene samples. All s.e.c. measurements were replicated twice, except for the last sample at $P_{\text{hydrogen}} = 0$ psi and $T = 70$°C, which was analysed only once.

Table 3 Molecular weight averages and polydispersities of polypropylene (measured by high temperature s.e.c.)

P_{H_2}(psi)	T(°C)	M_n	M_w	PDI
10	50	49 300 ± 760	226 700 ± 15 000	4.60 ± 0.24
10	60	38 100 ± 4100	166 500 ± 20 800	4.36 ± 0.07
10	70	33 200 ± 120	145 600 ± 2200	4.39 ± 0.05
5	60	57 400 ± 4400	248 600 ± 9500	4.34 ± 0.16
5	70	55 700 ± 3700	225 200 ± 9200	4.04 ± 0.11
0	50	301 300 ± 11 600	581 000 ± 17 200	1.93 ± 0.14
0	60	243 900 ± 12 500	536 900 ± 24 100	2.2 ± 0.15
0	70	165 500	434 800	2.59

Table 4 TREF fractionation results for polypropylene made at 70°C and partial pressure of hydrogen of 5 psi

Fraction #	ΔT (°C)	Sample weight (g)	% Wt
0	RT	0.213	0.6
1	RT–40	0.0179	0.5
2	40–90	0.0566	1.7
3	90–100	0.2416	7.1
4	100–105	0.1149	3.4
5	105–110	0.4499	13.3
6	110–115	0.7780	23.0
7	115–120	0.7157	21.2
8	120–125	0.9315	27.6
9	125–130	0.0128	0.4
10	130–140	0.0414	1.2
Total polymer recovered		3.3816	
Total polymer injected		3.45	
Efficiency		98%	

RT, room temperature; efficiency = total polymer recovered/total polymer injected × 100

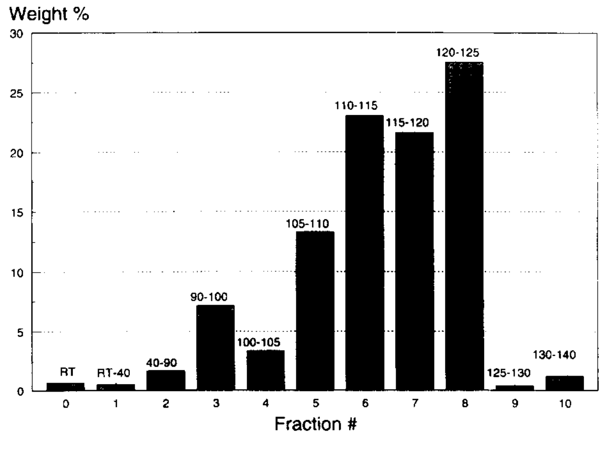

Figure 7 Preparative TREF profile of polypropylene made at 70°C and hydrogen partial pressure of 5 psi (legends on top of bars indicate the temperature interval, in °C, in which the fraction was obtained

As expected, the molecular weight averages of polypropylene produced at any hydrogen pressure decrease with increasing temperature, because of the normally higher activation energies for chain transfer than for propagation reactions. Polydispersities, however, do not change appreciably with polymerization temperature when hydrogen is present in the reactor.

Surprisingly, polypropylene made in the absence of hydrogen shows a very narrow polydispersity for a polyolefin made with a heterogeneous Ziegler–Natta catalyst. The polydispersity of those samples also increases slightly with increasing temperature.

Table 4 and *Figure 7* show the TREF profile of polypropylene made at a polymerization temperature of 70°C and a partial pressure of hydrogen of 5 psi. As can be seen, although most of the polymer is recovered between 100 and 125°C, some fractions can be collected either above or below this temperature range. Since there is only one monomer unit type, and ruling out the effect of molecular weight on TREF separation[11], the fractionation should be solely controlled by the stereo- and regio-regularity of the chains.

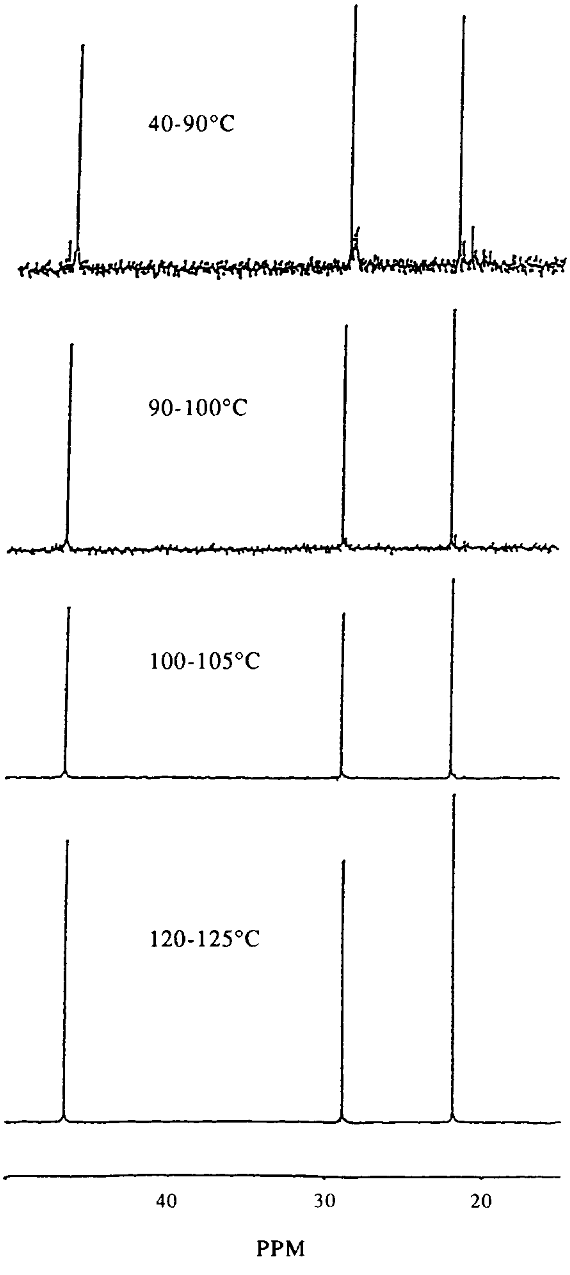

Figure 8 ^{13}C n.m.r. of TREF fractions of polypropylene

This broad elution profile agrees with the hypothesis of multiple site types on the catalyst, since sites of different types would likely have different stereochemical control.

Figure 8 shows the ^{13}C n.m.r. spectra of some TREF fractions. ^{13}C n.m.r. spectra of pure isotactic polypropylene should have only three single peaks, one for each nonequivalent carbon type in the chain (methylene, methine, and methyl)[8]. The TREF fraction obtained in the temperature interval 40–90°C shows several secondary peaks associated with stereoirregularities in the methyl region. Those peaks gradually disappear from the spectrogram for TREF fractions obtained at higher temperatures, which indicates that the fractionation mechanism is mainly regulated by the stereoregularity of the polypropylene chains.

Figure 9 and *Table 5* present the preparative TREF profile for polypropylene produced in absence of hydrogen. This profile is remarkably different from the one shown in *Figure 7* when the partial pressure of hydrogen was 5 psi. Almost no polymer is recovered below 110°C and practically all polymer elutes from the column between 110–135°C.

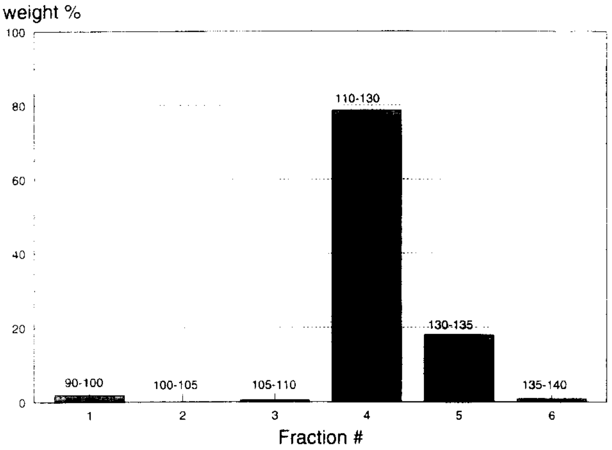

Figure 9 Preparative TREF profile of polypropylene made at 70°C in the absence of hydrogen (legends on top of bars indicate the temperature interval, in °C, in which the fraction was obtained)

Table 5 TREF fractionation results for polypropylene made at 70°C in the absence of hydrogen

Fraction #	ΔT (°C)	Sample weight (g)	% Wt
1	90–100	0.0695	1.9
2	100–105	0.0031	0.1
3	105–110	0.0201	0.5
4	110–130	2.9400	78.6
5	130–135	0.6744	18.0
6	135–140	0.0320	0.9
Total polymer recovered		3.7391	
Total polymer injected		4.00	
Efficiency		93.5%	

RT, room temperature; efficiency = total polymer recovered/total polymer injected × 100

DISCUSSION

The effect of hydrogen on the rate of olefin polymerization with Ziegler–Natta catalysts is rather complex and governed by mechanisms not fully elucidated[12,13]. Depending on the type of catalyst, cocatalyst, monomer, and polymerization conditions, the polymerization rate can either decrease[14–19], increase[19–25], or remain unaffected[10,19,26], in the presence of hydrogen. The reversibility of the hydrogen effect on the polymerization rate has also been noted by Natta[14].

Guastalla and Giannini[19] studied the effects of hydrogen on the polymerization rate of propylene and ethylene using a $MgCl_2$ supported catalyst. It was found that the presence of hydrogen generally increased the rate of polymerization of propylene, but decreased the rate of ethylene polymerization. At low polymerization temperatures (17°C), however, the rate of propylene polymerization was unaffected by the presence of hydrogen. No explanation was proposed to account for this behaviour.

According to Natta[14] and also Soga and Sino[18], the decrease in polymerization rate caused by hydrogen is due to a slow addition of the monomer to the catalyst–hydrogen bond formed in the step of chain transfer to hydrogen.

Several hypotheses have been proposed to account for the enhancement of the polymerization rate caused by hydrogen. Okura *et al.*[21] suggested that hydrogen and cocatalyst interact to further reduce the catalytic surface, forming new active sites not available when the cocatalyst is the single oxidizing agent. The formation of additional active sites has also been proposed by Buls and Higgins[24].

Pijpers and Roest[23] explained the increase in polymerization rate in terms of a complexation mechanism between the active centre and the dead polymer chain. The rate of polymerization in the absence of hydrogen is lower because polymer chains terminated by β-hydride elimination possess a terminal double bond that can interact with the transition metal at the active centre and compete with or prevent monomer insertion. On the other hand, chain ends of polymers terminated by transfer to hydrogen are saturated and cannot complex with the active site. Alternatively, the decrease in molecular weight caused by hydrogen could also facilitate chain migration from the active sites, thus favouring monomer diffusion through the polymer layer[27]. Both hypotheses have been contested by Barbé *et al.*[28].

Ross[25] proposed a dual mechanism to explain the rate enhancement-lowering effect of hydrogen: atomic hydrogen would be responsible for polymerization inhibition, while molecular hydrogen, particularly at high monomer and hydrogen concentrations, would account for the formation of new active sites, thus increasing the polymerization rate. This model would explain the discrepancy between the rate-enhancement effect observed by Guastalla and Giannini[19] (polymerization pressure of 3–4 $\mathrm{kg\,cm^{-2}}$) and Soga and Sino[18] (polymerization carried out at atmospheric pressure). However, some recent polymerization data of ethylene using a supported $MgCl_2$ catalyst contradict this hypothesis. Marques *et al.*[26] reported that the rate of ethylene polymerization is enhanced by hydrogen at pressures below 2 bars, but that higher hydrogen pressures first lower and then do not alter the rate of polymerization.

The enhancement in the rate of propylene polymerization observed in this work can therefore be related to similar observations in the literature. However, to our knowledge, this is the first time that combined evidence from polymerization kinetics and polymer microstructure characterization is used to analyse this phenomenon.

Although there is not significant experimental support for this hypothesis, apparently hydrogen interacts with the catalyst surface, probably with help of the monomer, creating more and different active site types, thus increasing the rate of propylene polymerization. The reversibility of the hydrogen effect can also be explained by this hypothesis. When hydrogen is removed from the reactor, the hydrogen-activated active sites lose their activity and, consequently, the polymerization rate decreases. If hydrogen is admitted again to the reactor, the hydrogen-activated sites become available once more, increasing the rate of polymerization. Additional support for this hypothesis comes from the MWDs of polymers made in the presence and absence of hydrogen.

Considering the MWDs measured by s.e.c., a possible explanation for the narrowing of the MWD of polypropylene produced without hydrogen is that some site types are active only in the presence of hydrogen. This hypothesis is clearly supported by the decrease in catalytic activity observed when hydrogen is removed from the polymerization reactor.

Therefore, for propylene polymerization with this catalytic system, hydrogen seems to activate site types that are dormant in its absence, increasing the catalyst activity and broadening the MWD of the formed polymer.

The broad TREF profile of polypropylene samples produced in the presence of hydrogen agrees with the hypothesis of multiple site types on the catalysts, since sites of different types would be likely to have different stereochemical control.

In the same way, the narrow TREF profile of polypropylene obtained in the absence of hydrogen agrees well with its s.e.c. analysis. The narrow MWDs observed for this polymer indicate that there are only a few active site types. Few site types imply smaller variances in molecular weight and stereoregularity distributions, and therefore a narrow TREF profile.

These results are also in good agreement with recent works in the mathematical modelling of MWD and TREF[4,5].

Finally, it should be pointed out that polypropylene synthesized with a catalyst system having multiple site types may have to be considered a complex polymer in the context of s.e.c. analysis. For a complex polymer, a unique relationship for mean square radius of gyration of a polymer chain in the s.e.c. mobile phase with polymer molecular weight may not exist[29].

CONCLUSION

The presence of hydrogen during the polymerization of propylene with a conventional heterogeneous Ziegler–Natta catalyst was found to increase the rate of propylene polymerization by creating new active site types. This was clearly shown using s.e.c., TREF, and ^{13}C n.m.r. analyses of the polypropylenes. It appears that this phenomenon of rate enhancement caused by hydrogen via the generation of new active site types has never been confirmed with TREF/s.e.c./^{13}C n.m.r. analysis of the product polymer, prior to this investigation.

REFERENCES

1 Elias, H. G. in 'Ullmann's Encyclopedia of Industrial Chemistry' (Eds B. Elvers, S. Hawkins and G. Schultz), Vol. A20, VCH Publishers, New York, 1992, p. 543.
2 Whiteley, K. S., Heggs, T. G., Koch, H., Mawer, R. L. and Immel, W. in 'Ullmann's Encyclopedia of Industrial Chemistry', (Eds B. Elvers, S. Hawkins and G. Schultz), VCH Publishers, New York, 1992, p. 487
3 Soares, J. B. P. and Hamielec, A. E. *Polym. Reac. Eng.* 1955, **3,** 261
4 Soares, J. B. P. and Hamielec, A. E. *Polymer* 1995, **36,** 2257
5 Soares, J. B. P. and Hamielec, A. E. *Macromol. Theory Simul.* 1995, **4,** 305
6 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953, p. 568.
7 Soares, J. B. P. and Hamielec, A. E. *Polymer* 1995, **36,** 1639
8 Randall, J. C. 'Polymer Sequence Distribution. Carbon-13 NMR Method', Academic Press, New York, 1977
9 Soares, J. B. P. PhD Thesis, McMaster University, Hamilton, Ontario, 1994
10 Yuan, H. G., Taylor, T. W., Choi, K. Y. and Ray, W. H. *J. Appl. Polym. Sci.* 1982, **27,** 1691
11 Wild, L. *Adv. Polym. Sci.* 1990, **98,** 1
12 Boor, J., Jr. 'Ziegler-Natta Catalysts and Polymerization' Academic Press, New York, 1979
13 Keii, T. in 'Transition Metal Catalyzed Polymerization' (Ed. R. P. Quirk), Harwood, New York, 1988, p. 84.
14 Natta, G. *Adv. Catal.* 1959, **11,** 1
15 Berger, M. N. and Grieveson, B. M. *Makromol. Chem.* 1965, **83,** 80
16 Keii, T. 'Kinetics of Ziegler-Natta Polymerization', Kodansha, Tokyo, 1972
17 Bohm, L. L. *Makromol. Chem.* 1981, **182,** 3291
18 Soga, K. and Sino, T. *Polym. Bull.* 1982, **8,** 261
19 Guastalla, G. and Giannini, U. *Makromol. Chem. Rapid Commun.* 1983, **4,** 519
20 Rayner, L. S. *Commun. J. Polym. Sci. Part C* 1964, **4,** 125
21 Okura, I., Kojima, A., Soga, K. and Keii, T. *J. Polym. Sci., Part A-1* 1970, **8,** 2717
22 Mason, C. D. and Schaffhausen, R. J. *J. Polym. Sci.* 1971, **B9,** 661
23 Pijpers, E. J. and Roest, B. C. *Eur. Polym. J.* 1972, **8,** 1151
24 Buls, V. W. and Higgins, T. L. *J. Polym. Sci., Polym. Chem. Edn* 1973, **11,** 925
25 Ross, J. F. *J. Polym. Sci., Polym Chem. Edn* 1984, **22,** 2255
26 Marques, M. M. V., Nunes, P. C., Tait, P. J. T. and Dias, A. R. *J. Polym. Sci., Polym. Chem. Edn.* 1993, **31,** 209
27 Boucheron, B. *Eur. Polym. J.* 1975, **11,** 131
28 Barbé, P. C., Cecchin, G. and Noristi, L. *Adv. Polym. Sci.* 1987, **81,** 1
29 Hamielec, A. E. and Ouano, G. *J. Liq. Chromatogr.* 1978, **1,** 111