Polymer Microstructure as a Probe into Hydrogen Activation Effect in *ansa*-Zirconocene/Methylaluminoxane Catalyzed Propene Polymerizations

Andrew Carvill, Incoronata Tritto, Paolo Locatelli, and Maria Carmela Sacchi*

Istituto di Chimica delle Macromolecole del C.N.R., Via E. Bassini 15, 20123 Milano, Italy

Received June 2, 1997; Revised Manuscript Received August 8, 1997[⊗]

ABSTRACT: Polypropenes were prepared, both in and without the presence of molecular hydrogen, using the six *ansa*-zirconocene catalysts *rac*-Et(Ind)$_2$ZrCl$_2$ (**I**), *rac*-Et(IndH$_4$)$_2$ZrCl$_2$ (**II**), *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$(**III**), *rac*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ (**IV**), *rac*-Me$_2$Si(Benz[*e*]Ind)$_2$ZrCl$_2$(**V**), and *rac*-Me$_2$Si(2-Me-Benz[*e*]Ind)$_2$ZrCl$_2$ (**VI**) and also Cp$_2$ZrCl$_2$ (**VII**) [Ind = indenyl], under standardized conditions (0.40 bar partial pressure of propene in toluene solution, at 30 °C, zirconocenes activated by methylaluminoxane). The microstructures of the polymers were investigated in detail by using ^{1}H and ^{13}C NMR and GPC, and relationships between catalyst structures and polymer microstructural features are discussed. Hydrogen was found to activate all of the catalysts to differing degrees. Trends in hydrogen activation were compared with trends in (a) the overall numbers of *n*-butyl terminals (resulting from chain transfer to hydrogen following secondary insertion), (b) the ratios, in the presence of hydrogen, of chain transfer to hydrogen to the other mechanisms which lead to renewed chain growth following secondary insertion, and (c) the ratios, in the presence of hydrogen, of sites following primary insertion to sites following secondary insertion. The absence of any clear correlations under these three headings leads to the conclusion that the release by chain transfer to hydrogen of resting states following secondary monomer insertion cannot be the only mechanism giving rise to hydrogen activation with these catalysts.

Introduction

The addition of molecular hydrogen as a chain-transfer agent to Ziegler−Natta catalyzed polymerizations of olefins has been an important method for the control of polymer molecular weights since the beginnings of the polyolefin industry in the early 1960s. It is known that the molecular weight control occurs by chain transfer to hydrogen, but the reasons for the additional effect of increase in catalyst activity which is observed in many cases in the presence of hydrogen are not yet clear. Many studies on heterogeneous Mg/Ti based catalysts[1−8] and a few on the newer homogeneous metallocene based catalysts[9−11] have been conducted and several theories on how hydrogen may effect an increase in polymer yields have been suggested, for example: (i) that hydrogen reacts with the surfaces of heterogeneous catalysts to increase the number of potentially active sites;[2] (ii) that hydrogen renews sites which have become deactivated to inert species such as metalallylics;[3] (iii) that hydrogen prevents the formation of unsaturated chain end groups which may act as poisons for the active sites;[4] (iv) that the hydrogen chain transfer reactions increase the overall activity of the catalyst by shortcutting the slow propagation steps which occur after isolated secondary insertions[5,6] (and possibly also after isolated stereoerrors in isotactic sequences[6c,7]), renewing fast propagation starting from metal-hydride species.

The analyses of regioerrors and chain-end groups in polymers made in the presence of hydrogen with both heterogeneous[1b,3d,4,5a,6,7] and homogeneous[8−10] catalysts have given some support to this last theory, since in the presence of hydrogen, *n*-butyl left-end groups (due to chain transfer to hydrogen after a secondary insertion) appear in far greater amounts relative to isobutyl groups (due to transfer to hydrogen after a primary insertion) than the ratios of enchained primary to secondary insertions in polymers made in the absence of hydrogen. However, the results so far published have been insufficient to show whether, as might be expected, there is a relationship between the numbers of *n*-butyl groups appearing and the degree of activation in the presence of hydrogen. We have hoped that studies based on the newer homogeneous metallocene based catalysts will shed new light on the topic. Indeed the microstructure of poly-α-olefins made with metallocene based catalysts is strongly influenced by the metal ligand structure.[11−13] This fact permits comparisons of the hydrogen effect between catalysts giving widely different polymerization behaviors, which was not possible with heterogeneous catalysts. Moreover, the relatively low molecular weights obtained by using these catalysts make possible a comprehensive analysis of chain-end groups which, with heterogeneous catalysts, was possible only on using ^{13}C enriched monomer or cocatalyst.

In the present study, we examine propene polymerizations conducted under uniform conditions (low propene pressure and low temperature) both with and without hydrogen, using the following seven different MAO activated zirconocene catalysts, *rac*-Et(Ind)$_2$ZrCl$_2$ (**I**), *rac*-Et(IndH$_4$)$_2$ZrCl$_2$ (**II**), *rac*-Me$_2$Si(Ind)$_2$ZrCl$_2$ (**III**), *rac*-Me$_2$Si(2-Me-Ind)$_2$ZrCl$_2$ (**IV**), *rac*-Me$_2$Si(Benz[e]-Ind)$_2$ZrCl$_2$ (**V**), and *rac*-Me$_2$Si(2-Me-Benz-[e]Ind)$_2$ZrCl$_2$ (**VI**) and Cp$_2$ZrCl$_2$ (**VII**). We present the results of a careful examination of the stereo- and regiospecificity of chain propagation and termination in the presence of the above-mentioned catalysts and of their relative activities both with and without hydrogen, with the aim of evaluating possible correlations between the variation of the polymer microstructure and the hydrogen activation effect.

Results and Discussion

General Observations. Table 1 shows the activities of the zirconocenes **I**−**VII** used and the principal

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1997.

S0024-9297(97)00773-0 CCC: $14.00

Table 1. Zirconocene Catalysts and Principal Polymer Properties

catalyst[a]/conditions[b]	$p(H_2)$, bar	yield,[c] g	activity,[c] kg PP/(mol Zr × h × bar Pr)	molecular weight and polydispersity			mmmm, %
				M_n (NMR)[d]	M_n (GPC)[e]	M_w/M_n (GPC)[e]	
$Et(Ind)_2ZrCl_2$ (**I**)	0	0.92	3,450	13,200	14,250	1.86	86.6
	0.21	3.43	12,800	5,040	4,070	1.92	87.3
$Et(IndH_4)_2ZrCl_2$ (**II**)	0	0.38	1,420	5,200	4,130	1.92	73.7
	0.21	1.00	3,750	2,460	1,970	1.66	74.5
$Me_2Si(Ind)_2ZrCl_2$ (**III**)	0	0.79	2,960	24,800	29,400	1.87	92.7
	0.21	1.63	6,100	7,000	5,830	2.04	93.8
$Me_2Si(2\text{-}Me\text{-}Ind)_2ZrCl_2$ (**IV**)	0	1.34	5,020	64,000	67,200	3.62	94.4
	0.21	3.43	12,860	17,900	18,440	1.97	93.5
$Me_2Si(Benz[e]Ind)_2ZrCl_2$ (**V**)	0	3.40	12,740	18,300	18,470	1.82	93.3
	0.21	5.82	21,800	6,300	5,040	2.00	94.5
$Me_2Si(2\text{-}Me\text{-}Benz[e]Ind)_2ZrCl_2$ (**VI**)	0	6.32	23,700	210,000	108,000	2.24	96.3
	0.21	10.2	38,200	9,900	10,800	2.29	96.2
Cp_2ZrCl_2 (**VII**)	0	0.42	1,570	400	ca. 320		ca. 5
	0.21	0.98	3,670	410	ca. 330		ca. 5
$Et(Ind)_2ZrCl_2$ (**I**)[g]	0	1.14	1,430	14,500	15,760	1.96	88.7
	0.21	3.57	4,460	7,900	6,980	1.93	89.1

[a] Ind = indenyl. [b] Polymerizations conducted for 1 h, at 0.40 bar partial pressure of propene, using 0.67 μmol of zirconocene/MAO (Zr:Al. = I:3000) in 100 cm^3 toluene at 30 ± 1 °C. [c] Based on mean yields of most active runs as described in Discussion. [d] Calculated as (10 000 × mol wt of monomer)/(0.5 × total terminals per 10 000 monomer insertions) based on NMR (Table 2). [e] Adjusted figures, based on polystyrene standards, see Experimental Section. [f] Calculated according to best fit of integrals of ^{13}C methyl signals for the four principal pentads to an enantiomorphic site control model.[17,27] [g] Polymerization conducted at propene partial pressure of 0.80 bar, with a less active (more aged) MAO sample.

Table 2. ^{13}C and ^1H NMR Analysis of Regioirregularities and Chain Terminals, per 10 000 Monomer Insertions[a,b]

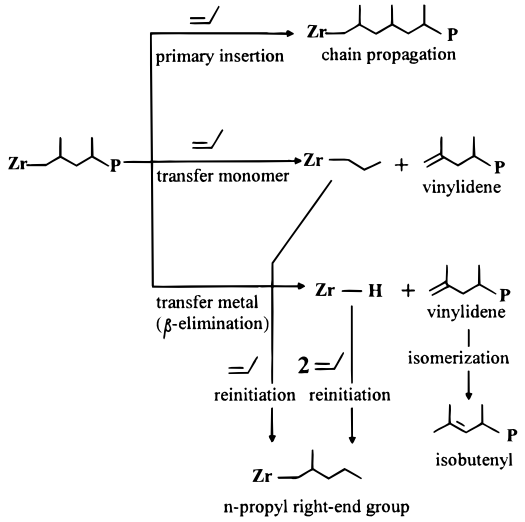
	enchained secondary insertions				terminals following 2,1 insertion		terminals following primary insertions			total all left-end terminals	right-end terminals (*n*-propyl[d])
catalyst[c]	2,1 erythro[d]	2,1 threo[d]	1,3[d]	total	2-butenyl[e]	*n*-butyl[d]	vinylidene[e]	isobutenyl[e]	isobutyl[d]		
I	29	26	15	69	11	nd	19	6	nd	36	28
I/H_2	nd	nd	trace	trace	trace	71	14	nd	trace	85	82
II	nd	nd	79	79	3	nd	71	nd	trace	74	87
II/H_2	nd	nd	5	5	nd	72	76	nd	43	191	151
III	27	14	3	44	7	nd	8	3	trace	18	16
III/H_2	nd	nd	trace	trace	trace	51	6	nd	7	64	56
IV	19	nd	nd	19	nd	nd	6	nd	trace	6	7
IV/H_2	6	nd	nd	6	nd	15	3	nd	11	29	18
V	63	11	3	77	13	nd	5	6	nd	24	22
V/H_2	25	6	trace	31	9	60	5	nd	trace	74	59
VI	32	nd	trace	32	nd	trace	~2	nd	nd	~2	~2
VI/H_2	17	nd	nd	17	nd	26	~4	nd	18	48	38
VII[f]				*f*	30	nd	1020	nd	trace	1,050	1,070
VII/H_2[f]				*f*	6	110	800	nd	120	1,036	1,000
I[g]	35	22	7	65	14	nd	14	6	nd	34	24
I/H_2[g]	18	14	trace	32	6	39	10	trace	nd	55	52

[a] nd: not detected. NMR signal/noise ratio imposed a baseline detectability limit of ca. 2 insertions per 10 000. [b] Trace: signals observed close to the limit of baseline detectability, could not be integrated reliably. [c] Conditions as shown in Table 1. [d] From ^{13}C NMR spectra (assignments refs 1b, 5a, 8−10, 28, 29). [e] From ^1H NMR spectra (assignments refs 10, 29). [f] Atactic oligomeric oil: no NMR signals (assignments ref 28) appearing to correspond to enchained 2,1 or 1,3 units could be identified. [g] Polymerization conducted at propene partial pressure of 0.80 bar, with a less active (more aged) MAO sample.

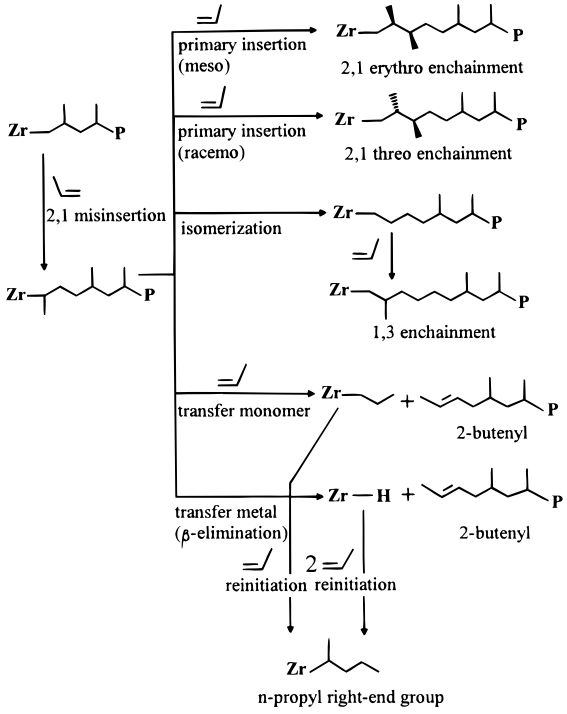
properties of the resulting polypropenes, both with and without hydrogen. Polymer yields for each catalyst were found to cover a relatively wide distribution.[14] Therefore, in order to have statistically relevant comparisons of catalyst activities, typically 12−15 polymerization runs with each zirconocene, with and without hydrogen, were conducted. The yields and activities given in Table 1 are means of the highest-yielding third of these runs. Thus they represent the mean *maximum* performances of each catalyst, both with and without hydrogen. A low partial propene pressure (0.40 bar, corresponding to a concentration of ca. 0.25 mol dm^{-3} Pr in toluene at 30 °C[15]) was chosen in order to make feasible the preparation of polypropenes under identical conditions using catalysts with a wide range of intrinsic activities, while avoiding the formation of too viscous polymerization mixtures with the most active catalysts. Preliminary tests showed that, under these conditions, the decreases in stereoregularity which occur at low propene concentrations[16,17] owing to isomerization of the Zr-bonded chain-end[18] were notable only for catalysts *rac*-$Et(Ind)_2ZrCl_2$ (**I**) and *rac*-$Et(IndH_4)_2ZrCl_2$ (**II**).

Table 2 shows the numbers (per 10 000 monomer insertions) of enchained regioirregularities and of all end-groups, based on analysis of the integrated signals due to the ^{13}C and ^1H NMR spectra of the polymers. Schemes 1−3 summarize the processes which are generally understood to lead to the formation of the regioirregularities and end-groups analyzed in Table 2. Schemes 1 and 2 show the microstructures which derive from primary and secondary monomer insertions, respectively, in the absence of hydrogen, while Scheme 3 shows the additional end-groups which result from chain transfer to hydrogen. All chain termination processes result in metal hydride or *n*-propyl species which are understood to form the basis of reinitiation of rapid chain growth, the new chains having *n*-propyl right-end groups. Thus, the numbers of *n*-propyl terminals should be equal to the numbers of all other (left-end) terminals together. The final columns of Table 2 show that this is in fact the case, but with the totals of left-end terminals generally appearing to exceed the numbers of *n*-propyls by 10−20%, likely due to errors

Scheme 1. Formation of Terminal Groups in Polypropene following Primary Monomer Insertion



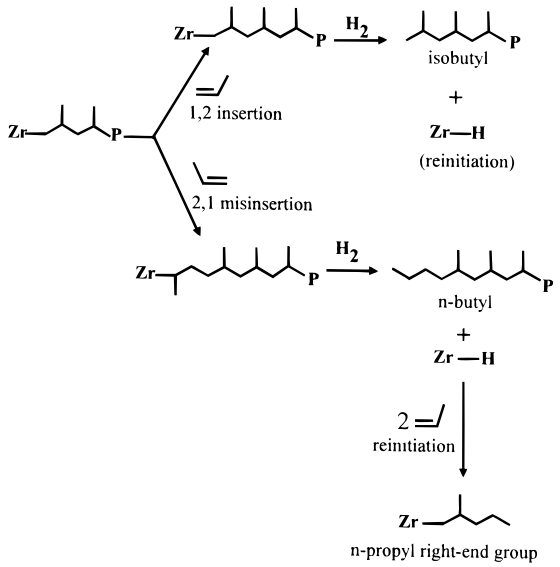
Scheme 2. Formation of Enchained Monomer Misinsertions and Terminal Groups in Polypropene, following Secondary Monomer Insertion



introduced by the summation of the integrals of left-end signals of low intensity.

Kinetic Runs. Activity during the course of each reaction was followed by monitoring the flow of propene into the reaction vessel, as the pressure was maintained by feeding propene. Figure 1 shows the activity curves for polymerizations, both with and without hydrogen, for three of the catalysts ranging from relatively inactive **II** to highly active **V**. From the figure, it can be seen that, both with and without hydrogen, there is with each catalyst a rapid increase in propene consumption during the first 5 min of reaction, reaching a maximum at ca. 8−12 min, and thereafter dropping to reach half the maximum consumption after 25−35 min. This shows that the falloff in activity was not due to increasing viscosity of the mixtures or to polymer precipitation, since the curves are similar for **V**, for which the mixture rapidly became a fairly viscous white suspension of polymer, and **II**, for which the mixture remained mobile

Scheme 3. Formation of Additional Terminal Groups in Polypropene, in the Presence of Hydrogen, following Primary and Secondary Monomer Insertion



and almost clear throughout the reaction. The curves also show that the increases in polymer yield with hydrogen are not due to increased duration of high activity, but rather to actual increases in activity. The decay trends observed are likely due to the fact that our MAO was freed from extractable $AlMe_3$ before reaction. The same kinetic profile has been observed, in ethylene polymerizations using zirconocenes/MAO where the MAO was similarly treated,[19] while steady-state build-up type curves were observed, in propene polymerizations at low monomer concentration, where MAO was used as provided.[10] It can be seen that the maximum activities are in each case about twice the average activities, based on polymer yield over 60 min, as quoted in Table 1.

Polymerizations in the Absence of Hydrogen. The tacticities, molecular weights, catalyst activities (Table 1), and distribution of regioirregularities/end-groups (Table 2) observed in the absence of hydrogen under our experimental conditions in general confirm trends observed previously at low monomer concentration. Thus, with respect to the now "classical" catalyst **I**, we have found the tetrahydro-derivative **II** to be notably less stereoselective and to give a higher number of chain terminations.[11] Both ethano-bridged catalysts **I** and **II** were found to be less stereoselective than the dimethylsilano-bridged catalysts **III**−**VI**.[12,13] Within the group of dimethylsilano-bridged catalysts **III**−**VI**, the addition of methyl substituents to the Zr-bonded rings in the 2-position (α to the bridge, catalysts **IV** *vs* **III** and **VI** *vs* **V**) was found, as previously,[10,12,13] to increase the molecular weight and stereoregularity of the polymers produced, as well as lessening by about half the number of enchained secondary insertions and almost eliminating the presence of 2-butenyl terminals. These results suggest that the benzanellation of the indenyl groups may reinforce these effects of the 2-methyl substituent, since the increases in molecular weight and stereoregularity were greater going from catalyst **V** to **VI** than going from **III** to **IV** (Table 1). The increase in molecular weight has been explained[10] as resulting from blockage, by the 2-methyl groups on the zirconocenes, of one of the pathways to chain transfer to monomer, which otherwise competes with chain propagation. Moreover, when the 2-methyl group is present on the zirconocenes (catalysts **IV** and **VI**),

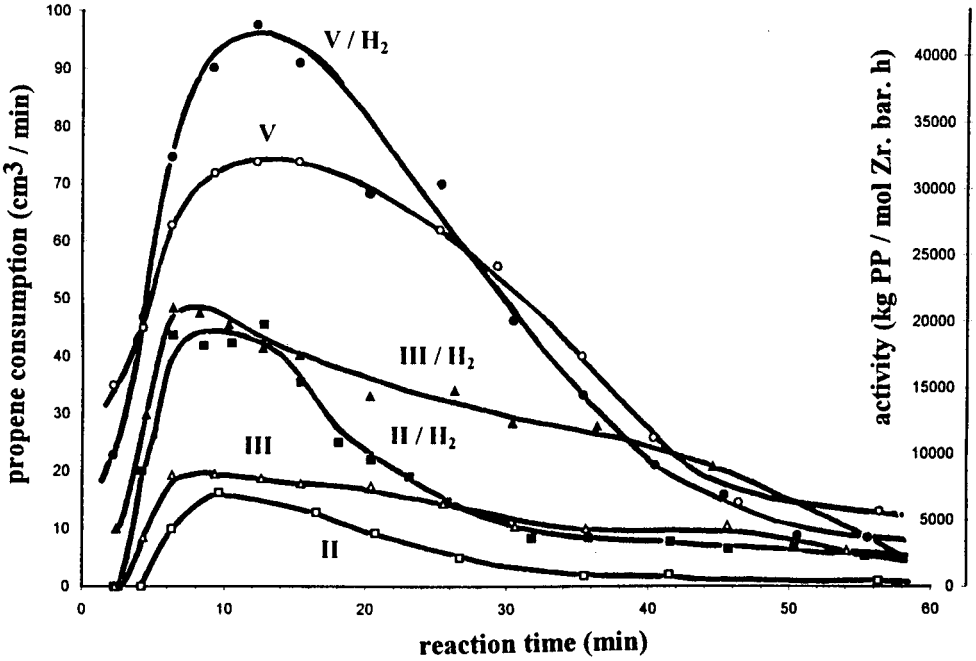


Figure 1. Propene consumption during reaction runs using selected MAO activated zirconocene catalysts, with and without hydrogen.

primary insertion after secondary insertion is only meso, giving exclusively erythro 2,1 enchainments[13] (Table 2).

There were, however, a few apparent departures from the trends observed previously, which we now briefly discuss. Catalyst **IV** was found to be almost twice as active as **III** and **VI** almost twice as active as **V** under our experimental conditions (Table 1) in contrast to previous observations made at higher propene concentrations, in which the opposite was true for both pairs of catalysts.[10,12,13] Relative activities similar to ours have been observed previously only at elevated polymerization temperatures, in the presence of relatively low propene concentrations, for the pair **V**, **VI**.[10] We attribute this inversion of the relative activities of the two pairs of catalysts to our low monomer concentration.[20] Recently published work has shown the relative activities of **V** and **VI** to be also strongly dependent on the MAO concentration.[21]

Another factor in which our results appeared to differ from trends previously reported was that with catalyst **II** at 30 °C, we found that almost all 2,1 insertions were isomerized to 1,3 (Scheme 2, Table 2) before continued chain propagation. This isomerization process was previously observed to go to completion only at elevated temperatures.[11] Here, our low monomer concentration has slowed the concentration-dependent process of primary insertion following secondary to such an extent that 2,1 to 1,3 isomerization, which is independent of monomer concentration, can go to completion even at low temperatures.[8]

Polymerizations in the Presence of Hydrogen. From Table 1 it can be seen that, as expected, the presence of hydrogen caused a lowering of polymer molecular weights. Except in the case of catalyst **VII**, with which the polymer molecular weight did not change, decreases by from ca. 50% to ca. 90% were observed. The stereoregularity of the polymers did not change substantially in the presence of hydrogen, with only slight increases being apparent in the case of some of the catalysts. This suggests that chain transfer to hydrogen following isolated stereoerrors was favored only slightly if at all. Figures 2 and 3 show relevant sections of ^{1}H and ^{13}C NMR spectra, respectively, of polymers prepared using catalysts **I**, **III**, and **V**, both with and without hydrogen.

Table 3 compares the increases in catalyst activity measured for each catalyst in the presence of hydrogen with parameters related to regioerrors (isolated secondary insertions) and chain termination. With all catalysts there was a decrease in the numbers of enchained secondary insertions (2,1 and 1,3) and in the numbers of 2-butenyl terminals (Table 2). Also, *n*-butyl terminals appeared in numbers which corresponded closely to the sum of the decreases in 2,1 and 1,3 enchainments and *n*-butenyl terminals (Figure 3, Table 3). This indicates that the presence of hydrogen did not affect overall numbers of secondary insertions with a given catalyst. It is noteworthy that, with Cp_2ZrCl_2 (**VII**), which gives atactic oligomers, a greater number of *n*-butyl terminals appeared in the presence of hydrogen than with any of the six isospecific bridged zirconocenes (Table 2), even though enchained secondary insertions were not observed in the absence of hydrogen. Our results therefore suggest that Cp_2ZrCl_2 (**VII**) may not be more regiospecific than the bridged isospecific catalysts as recently reported,[22] but instead that the secondary monomer insertions which occur with this catalyst lead to chain termination (forming 2-butenyl or, with hydrogen, *n*-butyl end-groups) rather than to enchained misinsertions.

If the principal factor involved in the hydrogen activation effect is the "fast release" by chain transfer to hydrogen of resting states following secondary insertion which are otherwise only slowly released (albeit at different rates for different catalysts[8,10]) by successive primary insertions or chain transfer to metal or monomer (Scheme 2), then one might expect to see some correspondence between the degree of activation and the overall numbers of *n*-butyl groups appearing with hydrogen. Table 3 (columns 3 and 6) shows that there is not such a correspondence. Indeed a lower number of *n*-butyl chain-end groups is produced with catalyst **IV** than with **VI**, while the activations follow the opposite trend. The same holds for the pairs **III**/**IV** and **III**/**V**.

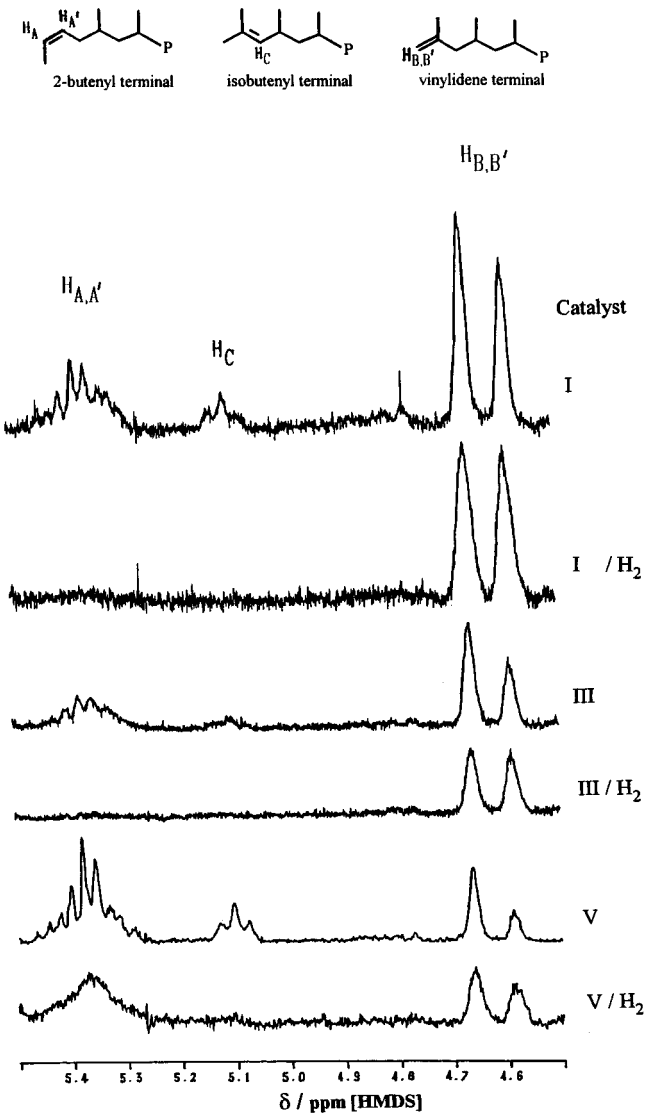


Figure 2. ^{1}H NMR spectra (270 MHz, olefinic region, assignments refs 10, 29) of polypropenes prepared by using selected MAO activated zirconocene catalysts, with and without hydrogen.

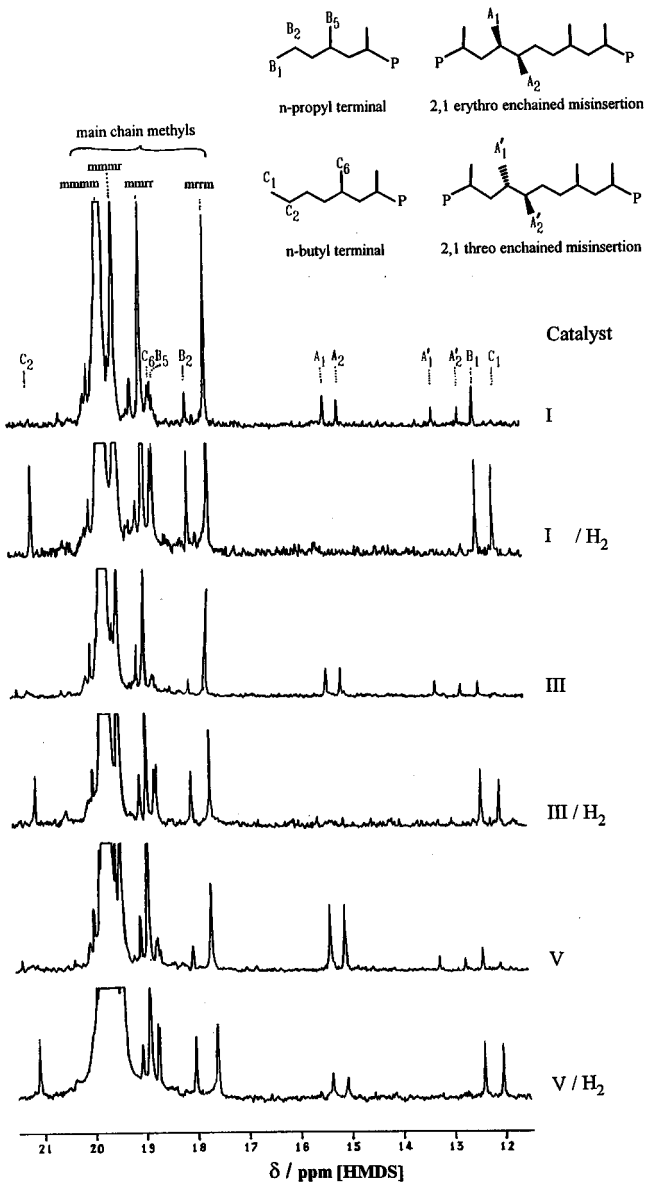


Figure 3. ^{13}C NMR spectra (67.89 MHz, expanded upfield region) of polypropenes prepared by using selected MAO activated zirconocene catalysts, with and without hydrogen.

Therefore we have also compared the degree of activation with the ratio, in the presence of hydrogen, of *n*-butyl groups to the sum of 2,1 and 1,3 enchainments plus 2-butenyl terminals. This ratio is a measure of the degree to which chain transfer to hydrogen competed with the combination of all other processes by which the active sites may become deblocked after a secondary insertion. If the renewal of chain growth after chain transfer to hydrogen is fast, then there should be a nearly linear relationship between this ratio and the degree of catalyst activation by hydrogen. From Table 3, columns 4 and 6, it may be seen that with some catalysts there was the expected correspondence between predominance of chain transfer to hydrogen (*n*-butyl) over the other processes (2,1 + 1,3 enchainment + 2-butenyl) and relatively high hydrogen activation (catalysts **I** and **II**) and between less complete predominance of chain transfer to hydrogen over the other processes and low activation (catalysts **V** and **VI**). However, the expected trend breaks down with catalyst **III**, for which activation was relatively low in spite of the high ratio of chain transfer to hydrogen to the other processes, and with catalyst **IV**, for which the opposite was true. The absence of a consistent relationship between this ratio and the degree of activation is highlighted by the results shown in the bottom rows of Tables 1−3. Here a higher propene/hydrogen ratio was used with catalyst **I**, and under these specific conditions the numbers of *n*-butyl terminals were *about equal* to the sum of enhanced secondary insertions and 2-butenyl terminals, meaning that the probability of chain transfer to hydrogen following secondary insertion was equal to that of all other processes leading to renewed chain growth. Indeed, if this (approximately 1:1) ratio of *n*-butyl to the other groups reflects the relative overall rates of the competing reactions, it is difficult to see how the observed activation in this case can derive at all from chain transfer to hydrogen. Surprisingly, here the activation effect was in fact only moderately less than in the previous trials with catalyst **I** described above, for which chain transfer to hydrogen was almost completely dominant over the other processes.[23]

Finally, the fifth column of Table 3 shows the ratios of *n*-butyl to isobutyl terminals in the polymers prepared with hydrogen. Since isobutyl groups result from chain transfer to hydrogen after primary insertion, under the assumption that the rates of chain transfer to hydrogen after primary or secondary monomer insertion are of

Table 3. Comparisons of Polymerization Results with and without Hydrogen

	secondary insertions and terminals			numerical ratios of terminals		catalyst activity
	1	**2**	**3**	**4**	**5**	**6**
cata-lyst[a]	total 2,1 + 1,3 ins + 2-butenyl/10 000 ins	decrease in 2,1 + 1,3 ins + 2-butenyl with H_2/10 000 ins	*n*-butyl appearing with H_2/10 000 ins	(*n*-butyl with H_2)/(2,1 + 1,3 ins + 2-butenyl with H_2)	(*n*-butyl with H_2)/(isobutyl with H_2)	(activity with H_2)/(activity without H_2)
I	80					
I/H_2	traces	80	71	≥20	≥20	3.73
II	82					
II/H_2	5	77	72	14	1.7	3.33
III	51					
III/H_2	traces	51	51	≥20	7.3	2.06
IV	19					
IV/H_2	6	13	15	2.5	1.4	2.56
V	90					
V/H_2	40	50	60	1.5	≥20	1.71
VI	32					
VI/H_2	17	15	26	1.5	1.4	1.61
VII						
VII/H_2			110		0.9	2.33
I[b]	79					
I/H_2[b]	38	41	39	1.0	≥20	3.13

[a] Conditions as shown in Table 1. [b] Polymerizations at 0.80 bar partial pressure; see Table 1.

the same magnitude, as seems reasonable for the small hydrogen molecule,[10,24] these ratios should reflect in a general way the ratios of zirconocene-polymeryl series in which the last monomer insertion was primary to those in which it was secondary, respectively. Subject to these considerations,[25] it can be seen that with catalysts **I**, **III**, and **V** the great majority of sites were in the "resting state" following secondary insertions, while with **II**, **IV**, **VI**, and **VII**, substantial proportions of the sites were in the "active" primary propagation mode. However, the tendencies in the hydrogen activation effects do not show any clear correspondence with these two groups of catalysts. Thus, **I** and **V** show the greatest and the second lowest activations, respectively, even though with both of these catalysts the great majority of sites are in the resting state following secondary insertion, while the pair **IV** and **VI** also show high and low activations, respectively, even though substantial proportions of sites are in the active (primary) propagation modes with these two catalysts.

Conclusions

Detailed analysis of the microstructure of polypropenes made using a range of *ansa*-zirconocene catalysts under standardized conditions, both with and without the presence of hydrogen, has been performed, with particular attention being paid to the events following isolated secondary monomer insertions. It was shown that, while hydrogen activated all of the catalysts, the relationships between the amount of chain transfer to hydrogen after secondary insertions and the degree of catalyst activation were not sufficient entirely to explain the latter in terms of the former. Thus we conclude that, while the "release" of resting states in polymer growth following secondary insertion by chain transfer to hydrogen may in part explain the hydrogen activation effect with these catalysts, there is most probably at least one other mechanism involved. We are currently investigating, with the same group of catalysts, the possibility that some type of catalyst deactivation by products of the polymerization reaction, which is lessened or suppressed by hydrogen, may also be responsible for the observed activation.

Experimental Section

Catalyst Preparation and Polymerizations. All operations were carried out under a dry nitrogen atmosphere by using drybox and standard vacuum Schlenk techniques. Nitrogen, hydrogen, and propene were purified by passage through columns of BASF RS-11 (Fluka) and Linde 4-Å molecular sieves. Methylaluminoxane (MAO, 30% w/w toluene solution, Schering) was used after removing all volatiles and drying the resulting white powder in vacuum (12 h, room temperature, 0.1 mbar). Toluene was dried by distillation from molten sodium under purified nitrogen. Zirconocene catalysts were used as obtained from commercial sources (Witco) or as kindly supplied by Prof. H. H. Brintzinger. Catalyst/cocatalyst solutions were prepared typically by dissolving 5 μmol of the zirconocene and 15 mmol of MAO (based on $Al(O)CH_3$, 58 g/mol) in 10 cm^3 of toluene. These solutions were stored in the dark at −15 °C and were generally found to retain constant activity over at least 6−8 days. In a typical polymerization reaction, 1.33 cm^3 of the above solution (=0.67 μmol of zirconocene + 2000 μmol of MAO) were added to 100 cm^3 of freshly distilled toluene at 30 °C in a 250-cm^3 round-bottomed flask equipped with an oil-filled glass finger for thermal contact between thermometer and solution, a gas inlet with stopcock, and a 1-in. oval-shaped stir bar. The solution was degassed by rapid stirring for several short intervals under vacuum, and hydrogen was then added to bring the total pressure to 250 mbar at equilibrium (=210 mbar partial pressure of hydrogen). Total pressure was then brought successively to 720 mbar with nitrogen and then rapidly to 1120 mbar with propene. (In polymerizations without hydrogen, pressure was initially brought to 720 mbar by using nitrogen only.) Equilibrium concentration of propene in solution was achieved within 3−4 min, by rapid stirring (ca. 1200 cycles per min), which was maintained throughout the reaction period. Total pressure was maintained at 1120 mbar throughout the polymerization by feeding propene, and the consumption of propene in the reactor was monitored by a fluximeter. Propene consumption data[26] were converted into instantaneous catalyst activities (Figure 1) on the basis that 1 cm^3 Pr/min (flow measured at 1120 mbar and 20 °C) is approximately equivalent to a consumption of 435 kg of Pr/mol of Zr × bar × h (reaction with 0.67 μmol of zirconocene, at 0.40 bar partial pressure of Pr). The temperature of the reaction mixture was maintained at 30 ± 1 °C throughout the reaction by means of a stirred water bath. At the beginning of the more active polymerizations, a temperature difference of up to 6 °C between bath and reactor was necessary in order to absorb the heat of reaction while maintaining the reaction temperature at 30 °C, and this difference was gradually lessened as the reaction activity diminished. Reactions were stopped at 60 min by addition of a small amount of ethanol, and polymers were precipitated by addition of the whole reaction mixture to methanol (600 cm^3) to which concentrated hydrochloric acid (5 cm^3) had been added. The precipitated polymer was washed with methanol and dried firstly in air and then under vacuum at 60 °C to constant weight.

NMR Analysis. ^1H and ^{13}C NMR spectra were recorded in pulsed Fourier transform mode at 270 and 67.89 MHz, respectively, on a Bruker 270 spectrometer in $C_2D_2Cl_4$ solution

at 107 °C. Chemical shifts were referred to internal hexamethyldisiloxane (δ HMDS $\approx$ δ TMS minus 2.0 ppm for ^{13}C, δ HMDS $\approx$ δ TMS minus 0.06 ppm for ^{1}H). For ^{1}H spectra, typically 500 free induction decays were accumulated. ^{13}C spectra were measured with composite pulse decoupling to remove ^{13}C−^{1}H couplings, the pulse angle was 90°, the pulse repetition time was 27 s, and typically 5000 free induction decays were stored in 32 000 data points using a spectral window of 4950 Hz.

Gel Permeation Chromatography. Molecular weights of the polymers were determined by gel permeation chromatography in *o*-dichlorobenzene at 135 °C, using a Waters 150-C gel permeation chromatograph equipped with four Styragel HT columns (10^6, 10^5, 10^4, and 10^3-Å pore size). The universal calibration curve, as a polynomial third order fit, was constructed by means of 16 polystyrene standards with narrow molecular weight distributions (M_w ranging from 580 to 5 480 000).

Acknowledgment. We are particularly grateful to Professor Umberto Giannini for many stimulating and helpful discussions. Thanks are due to Mr. Giulio Zannoni for valuable assistance in obtaining the NMR spectra and to Mr. Alberto Schieroni for GPC measurements. Financial help from the EC Project "Human Capital and Mobility", Network No. ERBCHGECT 930/58 OPTMO (olefin polymerization with catalysts based on transition metals and organometallics) is gratefully acknowledged.

References and Notes

(1) (a) Guastalla, G.; Giannini, U. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 519. (b) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Macromolecules* **1988**, *21*, 2675.

(2) (a) Parsons, I. W.; Al-Turki, T. M. *Polym. Commun.* **1989**, *30*, 72. (b) Kioka, M.; Kashiwa, N. *J. Macromol. Sci.-Part A (Chem.)* **1991**, *A28*, 865.

(3) (a) Spitz, R.; Masson, P.; Bobichon, C.; Guyot, A. *Makromol. Chem.* **1988**, *189*, 1043. (b) Spitz, R.; Masson, P.; Bobichon, C.; Guyot, A. *Makromol. Chem.* **1989**, *190*, 717. (c) Guyot, A.; Spitz, R.; Dassaud, J. P.; Gomez, C. *J. Mol. Catal.* **1993**, *82*, 29. (d) Bukatov, G. D.; Gancharov, V. S.; Zakharov, V. A. *Macromol. Chem. Phys.* **1995**, *196*, 1751.

(4) Imaoka, K.; Ikai, S.; Tamura, M.; Yoshikiyo, M.; Yano, T. *J. Mol. Catal.* **1993**, *82*, 37.

(5) (a) Kojoh, S.; Kioka, M.; Kashiwa, N.; Itoh, M.; Mizuno, A. *Polymer* **1995**, *36*, 5015. (b) Mori, H.; Tashino, K.; Terano, M.; *Macromol. Chem. Phys.* **1995**, *196*, 651.

(6) (a) Chadwick, J. C.; Miedema, A.; Sudmeijer, O. *Macromol. Chem. Phys.* **1994**, *195*, 167. (b) Albizzati, E.; Giannini, U.; Balbontin, G.; Camurati, I.; Chadwick, J. C.; Dall'Occo, T.; Dubitsky, Y.; Galimberti, M.; Morini, G.; Maldotti, A. *J. Polym. Sci.*, in press. (c) Chadwick, J. C.; van Kessel, G. M. M.; Sudjmeier, O. *Macromol. Chem. Phys.* **1995**, *196*, 1431.

(7) Chadwick, J. C.; Morini, G.; Albizzati, E.; Balbontin, G.; Mingozzi, I.; Cristofori, A.; Sudmeijer, O.; van Kessel, G. M. M. *Macromol. Chem. Phys.* **1996**, *197*, 2501.

(8) Busico, V.; Cipullo, R.; Chadwick, J. C.; Modder, J. F.; Sudjmeier, O. *Macromolecules* **1994**, *27*, 7538.

(9) Tsutsui, T.; Kashiwa, N.; Mizuno, A. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 565.

(10) Jüngling, S.; Mülhaupt, R.; Stehling, U.; Brintzinger, H. H.; Fischer, D.; Langhauser, F. *J. Polymer Sci. Part A* **1995**, *33*, 1305.

(11) Schupfner, G.; Kaminsky, W. *J. Mol. Catal. A.* **1995**, *C102*, 59.

(12) Spaleck, W.; Küber, F.; Winter, A. Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954.

(13) Stehling, U.; Diebold, J.; Kirsten, R.; Röll.; Brintzinger, H. H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964.

(14) Molecular weights and polydispersities (GPC), however, were found to cover much narrower ranges, characteristic of each zirconocene, indicating that the variations in yield within a single set of reaction conditions (i.e., particular zirconocene with or without hydrogen) were due to variations in the amounts of actually active catalyst, and not to changes in the character of the reaction.

(15) (a) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer: New York, 1985. (b) Forlini, F., unpublished results.

(16) (a) Busico, V.; Cipullo, R. *J. Am. Chem. Soc.* **1994**, *116*, 9329. (b) Busico, V.; Cipullo, R. *Macromol. Symp.* **1995**, *89*, 277.

(17) Resconi, L.; Fait, A.; Piemontesi, F.; Colonnesi, M.; Rychlicki, H.; Ziegler, R. *Macromolecules* **1995**, *28*, 6667.

(18) Leclerc, M. K.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1996**, *118*, 9024.

(19) (a) Srinvasa Reddy, S.; Shashidhar, G.; Sivaram, S. *Macromolecules* **1993**, *26*, 1180. (b) Rieger, B.; Janiak, C. *Angew. Makromol. Chem.* **1994**, *215*, 35.

(20) The fact that **V** was more active than **VI** at higher concentrations could be explained by the process of monomer-assisted chain transfer to monomer, which has been found to occur following secondary insertions with **V** but to be blocked by the 2-methyl groups present on the ligand in **VI**.[10] We attribute our observations to the fact that this process, which favors the activity of **V** over that of **VI** but which is strongly dependent on monomer concentration, should become relatively unimportant at low monomer concentrations. This explanation is supported by previous observations at 40 °C, in which **V** was more active than **VI**, but in which the difference in activity diminished with lessening monomer concentration.[10] Therefore, it may be that under our conditions the main factor governing the relative activities of **V** *vs* **VI**, is simply an inverse relationship between activity and numbers of secondary insertions (Table 2). These same arguments may also explain the similar reversal of the relative activities of the pair of catalysts **III** and **IV**, on going from high monomer concentrations (refs 12 and 13) to our conditions of low concentration (Tables 1 and 2).

(21) Koltzenburg, S. *J. Mol. Catal. A: (Chem.)* **1997**, *116*, 355.

(22) Guerra, G.; Cavallo, L.; Corradini, P.; Longo, P.; Resconi, R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, *37*, 469.

(23) This consideration is in agreement with results of Tsutsui and Kashiwa, who in a series of propene polymerizations with catalyst **I** found that the maximum activation effect (ca. 3.5-fold) was already reached under conditions of low partial pressure of hydrogen, in which the numbers of 2,1 and 1,3 enchained insertions and 2-butenyl terminals observable in the absence of hydrogen had been lessened by only 30%. Increasing further the partial pressure of hydrogen suppressed the remaining secondary enchainments and 2-butenyl terminals without causing any further activation.[9]

(24) (a) de Carvalho, A. B.; Gloor, P. E.; Hamielec, A. E. *Polymer* **1989**, *30*, 280. (b) Busico, V.; Cipullo, R.; Corradini, P. *Makromol. Chem. Rapid Commun.* **1993**, *14*, 97.

(25) The ratio of isobutyl to *n*-butyl groups cannot be assumed to be either equal to or directly proportional to the ratios of Zr-1,2 and Zr-2,1 units present, since there are two competing reactions involved in the formation of each of these terminals, namely, chain transfer to H_2 and monomer insertion. Even though it is reasonable to assume that the rates of chain transfer to H_2 from a Zr-2,1 unit and from a Zr-1,2 unit are of the same magnitude, it is also probable that monomer competes better with H_2 for coordination to the Zr-1,2 unit than it does to the Zr-2,1 unit. Therefore, the ratio of isobutyl to *n*-butyl terminals is probably less than the ratio of Zr-1,2 to Zr-2,1 sites present; i.e., the proportion of Zr-1,2 sites is underestimated. It is also probable that the differences in competitively between H_2 and monomer for Zr-1,2 and Zr-2,1 sites, and therefore the amount by which this reckoning underestimates the Zr-1,2 sites, would vary from one metallocene to another.

(26) The curves in Figure 1 were corrected for the rapid flow of propene into the reactor during equilibration of propene in solution in toluene (first 3−4 min) by subtracting from them the curve recorded for dissolution of propene in the absence of catalyst, under otherwise identical conditions.

(27) (a) van der Burg, M. W.; Chadwick, J. C.; Sudmeijer, O.; Tulleken, H. J. A. F. *Makromol. Chem., Theory Simul.* **1993**, *2*, 399. (b) Rieger, B.; Reinmuth, A.; Röll, W.; Brintzinger, H. H. *J. Mol. Catal.*, **1993**, *82*, 67.

(28) (a) Grassi, A.; Zambelli, A.; Resconi, L.; Albizzati, E.; Mazzochi, R. *Macromolecules* **1988**, *21*, 617. (b) Cheng, H. N.; Smith, D. A. *Macromolecules* **1986**, *19*, 2065. (c) Cheng, H. N. *Macromol. Symp.* **1994**, *86*, 77. (d) Tsutsui, T.; Mizuno, A.; Kashiwa, N. *Polymer* **1989**, *30*, 428.

(29) (a) Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 3356. (b) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Ziegler, R. *Organometallics* **1996**, *15*, 5046.

MA970773G