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Ethylene/α-olefins cooligomerization *versus* copolymerization by zirconocene catalysts

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Non-bridged zirconocene complexes activated with methylalumoxane can polymerize monoalkenes to high polymers with very high activity. The main control of molecular weight in these systems is due to β-H transfer from the growing chain, the effect becoming very remarkable in the case of substituted ethylene monomers and with increasing temperature. This work is mainly devoted to test the real capacity of the subject catalyst to produce structurally controlled oligomers from ethylene or ethylene/α-olefin mixtures in good yield by investigating the influence of different reaction parameters. On the basis of the relevant results obtained, conditions were identified favouring the cooligomerization of ethylene with propylene and higher α-olefins *versus* the formation of high molecular weight macromolecules. The role of reaction conditions (catalyst, cocatalysts, temperature, pressure, structure of comonomer and presence of hydrogen) on products structure and yield is discussed with reference to previously proposed chain propagation and chain transfer mechanisms. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Non-bridged zirconocene complexes, particularly bis(cyclopentadienyl)zirconium derivatives activated with methylalumoxane (MAO), are known to give polyethylene (PE) in high yield (up to 3×10^4 kg PE^{-1} g Zr h^{-1}) and molecular weight (MW) decreasing from 600 000 to 120 000 when the temperature is increased from 20 to 70°C[1]. On the other hand, higher MWs can be obtained with specifically designed metallocene ligands hindering β-H abstraction during the polymerization reaction[2]. Preparation of oligomeric olefins through metallocene catalysts has been described mainly as a tool for evaluating chain transfer mechanisms operating during polymerization and the consequent microstructure of products[3,4], though some efforts have also been recently made to establishing the effects of polymerization conditions on the properties of the products[5]. In addition, optically active terminal olefins were prepared by Kaminsky *et al.*[6] using conditions under which the transfer reaction was optimized.

The present paper shows the study of ethylene oligomerization with the aim of obtaining short chain liquid products under different catalytic and experimental conditions at usual polymerization temperatures also allowing copolymerization. The formation of low oligomers (C_4–C_{20+}) from ethylene and ethylene/α-olefin mixtures at temperatures higher than 100°C is described in a recent industrial patent[7]; at this high temperature often no polymerization occurs and different reaction mechanisms are probably involved.

In the present contribution the catalytic performance of three different metallocenes derived from Zr(IV) activated with methylaluminoxane (MAO) on the oligomerization of ethylene are compared under standardized conditions. The competitive formation of liquid oligomers *versus* solid high polymer has also been used to further elucidate the general mechanism of ethylene and α-olefins polymerization. The variables considered were mainly temperature, Al/Zr molar ratio and the presence of a α-olefin used as a comonomer, whilst the effects of interest were catalyst activity and average molecular weight or intrinsic viscosity of the products. A similar approach was followed by Kaminsky[8] to show that the growing chain end has a small influence on isotacticity. Indeed the oligomerization of 1-butene with optically active metallocenes allowed to demonstrate that each insertion step increases the stereospecificity to reach an asymptotic value.

The results are illustrated according to the type of monoalkene: thus after a section devoted to the comparison of the behaviour of ethylene and propylene, the influence of higher olefins as ethylene comonomers will be presented. Catalyst components and their preparation

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were selected in such a way that it could be assumed that the active molecules are 14-electron cationic transition metal complexes derived from alkylation and abstraction of chlorine atoms by MAO oligomeric species as has already been extensively studied[9,10].

EXPERIMENTAL

All operations were performed under a dry argon atmosphere. All solvents and liquid α-olefins were purified by refluxing over sodium/potassium alloy and subsequent distillation. The metallocene complexes chosen for this study were either prepared via published methods[2,11,12] or commercially available. Methylaluminoxane (MAO) was purchased from Witco (4.5 M solution in toluene). All other reagents were obtained from commercial sources and were used as received.

Polymerization experiments

The polymerizations were carried out in a 200 ml glass reaction vessel (Büchi) equipped with a temperature controller and a mechanical stirrer. The gaseous feed was continuously supplied into the reactor (containing 60 ml of toluene) at the desired pressure. In the copolymerizations, the required amount of α-olefin was introduced into the reactor just prior to catalyst addition adjusting the solvent volume in order to keep the total liquid volume constant at 60 ml. When required, hydrogen introduction was made immediately before monomer injection. The reactions were quenched by adding acidic water. When present the precipitated polymers were filtered, washed with *n*-pentane and dried under reduced pressure. The organic solutions were adequately extracted with iced water, dried on anhydrous Na_2SO_4 and submitted to gas chromatographic and mass spectrometry analysis. Specific reaction conditions may be found in the appropriate tables and in the text.

Products characterization

G.c.-m.s. analysis was performed on a Perkin-Elmer 910 quadrupole mass analyzer interfaced with a Perkin Elmer 8500 gas chromatograph carrying a DBI capillary column (length 30 m, film thickness 0.25 mm). The intrinsic viscosity was measured with a Ubbelhode type viscometer in decahydronaphthalene at 135°C and the viscosity average MWs of the samples were calculated accordingly[13].

I.r. and n.m.r. spectra were recorded using a Perkin-Elmer Mod. 1600 Series *FT*i.r. and Varian 200 MHz, respectively.

RESULTS AND DISCUSSION

Ethylene homopolymerization

A series of experiments of ethylene polymerization was carried out under standardized rather than optimized conditions, mainly to obtain coherent and comparable data for detecting the effect of the various parameters. Three catalyst precursors [bis(cyclopentadienyl)zirconium dimethyl ($Cp_2Zr(CH_3)_2$), bis(cyclopentadienyl)titanium dimethyl ($Cp_2Ti(CH_3)_2$) and *rac*-ethylene-bis(1-indenyl)-zirconium dichloride ($EBIZrCl_2$)] were employed. The following reaction conditions were used: temperature range from 20 to 100°C, ethylene pressure 1 bar, mol ratio MAO/Mt (Mt = Ti, Zr) 300–1000 (0.098 mmol ml^{-1} transition metal complex), duration time 1 h. Additional experiments were carried out with the same system and the contemporary use of triethyl aluminium (TEA) added as third component to the catalytic mixture in order to favour chain transfer (*Table 1*).

The study was initially performed in order to check the real possibility of controlling polyethylene MW by chain transfer reactions promoted by temperature raising and/or TEA addition. Each run resulted in exclusively polymeric products, having viscosity average molecular

Table 1 Polymerization of ethylene using a metallocene, MAO and TEA as catalytic system[a]

Run	Metallocene type	MAO/Mt Mole ratio	TEA/Mt Mole ratio	*T* (°C)	Productivity[b]	MW[c]
EM01	$Cp_2Zr(CH_3)_2$	300	—	20	74.8	52 000
EM02	$Cp_2Zr(CH_3)_2$	500	—	20	106.7	57 000
EM03	$Cp_2Zr(CH_3)_2$	1000	—	20	150.5	59 000
EM05	$Cp_2Zr(CH_3)_2$	300	—	80	99.4	7300
EM06	$Cp_2Zr(CH_3)_2$	500	—	80	150.5	4500
EM07	$Cp_2Zr(CH_3)_2$	1000	—	80	189.7	6200
EM08	$Cp_2Zr(CH_3)_2$	1000	—	100	0	—
EM04	$Cp_2Ti(CH_3)_2$	1000	—	20	49.8	28 000
EM09	$EBIZrCl_2$	1000	—	20	116.8	50 000
EM10	$Cp_2Zr(CH_3)_2$	1000	50	20	84.8	8600
EM11	$Cp_2Zr(CH_3)_2$	1000	100	20	62.9	6700
EM12	$Cp_2Zr(CH_3)_2$	1000	100	80	0	—
EM13	$Cp_2Zr(CH_3)_2$	1000	500	20	3.6	—
EM14	$Cp_2Zr(CH_3)_2$	1000	1000	20	0	—
EM21	$Cp_2Ti(CH_3)_2$	1000	200	20	10.0	5600
EM19	$EBIZrCl_2$	1000	100	20	100.3	5600
EM20	$EBIZrCl_2$	1000	200	20	96.7	6400

[a] In toluene with 1 bar ethylene, 5.9 μmol metallocene, duration 1 h

[b] kg PE mol^{-1} Mt h^{-1}

[c] Average molecular weight determined via viscosity measurements on the total product obtained in decalin at 135°C

weight (MW) in the range 4500–59 000 when using $Cp_2Zr(CH_3)_2$. The activity increased with increasing molar ratio MAO/transition metal (Mt), both at 20 and 80°C, though this parameter seemed not to influence the polymer MW, thus showing that MAO does not act in a significant way as chain transfer agent during ethylene polymerization[8,14]. A higher temperature led to a reduction of about one order of magnitude of the MW from 20 (run EM03) to 80°C (run EM07) with an appreciable increase of productivity, a further increase to 100°C (run EM08) caused a complete deactivation of the catalytic active sites. The influence of the metallocenic complex was evidenced by a sharp decrease in the activity of polymerization of $Cp_2Ti(CH_3)_2$ (run EM04) compared to that of $Cp_2Zr(CH_3)_2$ (run EM03) and to a lesser extent in the case of the bridged complex $EBIZrCl_2$ (run EM09), though none of them appeared to be active in reducing chain growth processes. The lower activity exhibited by the titanocene complex compared to that of the zirconocene has already been ascribed to the instability of the cationic active sites of Ti(IV), these are likely to reduce to Ti(III) species which are inactive under these conditions[15].

Adding TEA as a third component to the catalyst system mainly showed a marked diminution of the activity, which was characterized by a rapid collapse both for increasing TEA/Mt molar ratio and the temperature of reaction. The resulting polymers exhibited a reduced MW (about one order of magnitude). Even if TEA theoretically acts as chain transfer agent, its introduction in the reaction medium evidently also caused the deactivation of the metallocene complexes through bimolecular reactions[16]. In addition, the formation of EAO (ethylalumoxane) resulting from alkyl exchange reactions between MAO and TEA cannot be excluded, this would give much lower catalytic activity. The data reported in *Table 1* show that the typical transfer reactions occurring in Ziegler–Natta polymerization do not permit a good yield of liquid oligomers from ethylene, at least under the conditions adopted in this study. The reduction of an order of magnitude of MW from about 5×10^4 to 5×10^3 and a decreased catalytic activity were generally observed.

Successive experiments were then carried out with ethylene/hydrogen mixtures. Hydrogen has been extensively used as an effective chain transfer agent in α-olefins polyinsertion promoted by homogeneous catalysts, mainly for the understanding of the mechanism of the stereospecific polymerization[17,18]. Kaminsky and Lüker[19] first showed that PE molecular weight is reduced by the presence of hydrogen according to expectations. Using $Cp_2Zr(CH_3)_2$ and highly purified C_2H_4 with $C_2H_4/H_2 \leq 1$ at 20°C the solid polymer MW was further reduced about to 1000 and about 30% of the product consisted of liquid oligomers. A further reduction of MW was obtained by raising the temperature to 70°C; at this last temperature and C_2H_4/H_2 ratio of about 4, almost all liquid oligomers were obtained with an interesting productivity, $P_{C_2H_4} = 3$ atm (*Table 2*).

Table 2 Oligomerization and polymerization of ethylene using Cp_2ZrMe_2/MAO as a catalyst and hydrogen[a]

Run	$P_{C_2H_4}$ (bar)	P_{H_2} (bar)	T (°C)	Oligomers Productivity[b]	Polymer Productivity[b]	Polymer MW
HE01	5	1	20	0	567	4400
HE02	1	1	20	37	342	1600
HE03	0.3	0.7	20	107	293	1000
HE04	3	0.7	70	458	5	—

[a] In *n*-heptane, with 5.9 μmol metallocene, [Al]/[Zr] = 1000, duration 1 h
[b] $kg\,mol^{-1}\,Zr\,h^{-1}\,bar^{-1}$

Table 3 Oligomerization of propylene using different metallocenes and MAO as catalytic system[a]

Run	Metallocene	Al/Zr	T (°C)	P (bar)	Oligomers Productivity[b]	Oligomers Range
PM01	Cp_2ZrMe_2	300	20	1	16	C_6–C_{30+}
PM02	Cp_2ZrMe_2	1000	20	1	167	C_6–C_{30+}
PM03	Cp_2ZrMe_2	3000	20	1	700	C_6–C_{30+}
PM04	Cp_2ZrMe_2	3000	70	1	2350	C_6–C_{30+}
PM06[c]	$EBIZrCl_2$	3000	20	1	0	—
PM07	Ind_2ZrCl_2	1000	20	1	117	$>C_{30}$
PM08	Ind_2ZrCl_2	3000	20	1	983	$>C_{30}$
PM09	Ind_2ZrCl_2	3000	20	5	437	$>C_{30}$
PM10	Ind_2ZrCl_2	3000	70	1	1017	C_6–C_{30+}
PM11	Ind_2ZrCl_2	3000	70	5	526	C_6–C_{30+}
PM12	$Cp^*_2ZrCl_2$	1000	20	1	266	C_6–C_{24}
PM13	$Cp^*_2ZrCl_2$	3000	20	1	1200	C_6–C_{24}
PM14	$Cp^*_2ZrCl_2$	3000	20	5	914	C_6–C_{24}
PM15	$Cp^*_2ZrCl_2$	3000	70	1	762	C_6–C_{18}
PM16	$Cp^*_2ZrCl_2$	3000	70	5	900	C_6–C_{21}

[a] In toluene with 6.0 μmol metallocene, duration 1 h
[b] $kg\,PE\,mol^{-1}\,Zr\,h^{-1}$
[c] Isotactic polypropylene was obtained as the sole product with $2830\,kg\,PP\,mol^{-1}\,Zr\,h^{-1}$ productivity

Propylene oligomerization

The metallocene complexes used for these experiments were Cp_2ZrMe_2, $EBIZrCl_2$, bis(indenyl)zirconium dichloride (Ind_2ZrCl_2) and bis-(pentamethylcyclopentadienyl)zirconium dichloride ($Cp^*_2ZrCl_2$). The reactions were carried out with an Al/Zr molar ratio of 300–3000, at two different temperatures (20 and 70°C) and 1 or 5 bars propylene pressure (*Table 3*).

Whereas ethylene had given only solid polymers under the same conditions, propylene gave the exclusive formation of oligomers with average MW strictly dependent on the zirconium complex used at temperatures below 50°C. In the case of the bridged metallocene $EBIZrCl_2$ highly isotactic polypropylene was obtained and almost no oligomers. Experimental data showed that the products obtained in the presence of Cp_2ZrMe_2 were constituted by low MW olefinic hydrocarbons distributed in the gas chromatographically detectable range C_6–C_{30} (*Table 3*). On the other hand, in the case of Ind_2ZrCl_2 and $Cp^*_2ZrCl_2$ two results were found: the first metallocene produced only higher MW oligomers (not detectable via g.c.-m.s. analysis under our experimental conditions at $T = 50$–$270°C$), while the second was characterized by giving exclusively low MW oligomers whose quantitative determination was partially compromised because of their high volatility which is clearly shown by the oligomers distribution obtained with the three different catalysts. Electronic and steric effects of the organic ligands around the transition metal can be held to be responsible for this different behaviour[20]. Even if the productivity values are affected by the possible incomplete detection of volatile dimers, it is evident that an increase of the MAO/Zr ratio is accompanied by an increase of productivity with practically no effect on oligomer distribution. On the other hand, the increase of the temperature from 20 to 70°C mainly produces a MW decrease in all cases, even if the effect on productivity seems to be remarkable only for $Cp_2Zr(CH_3)_2$. It is of interest to note that an increase of propylene pressure from 1 to 5 bar does not seem to effect the MW.

The separation of the oligomeric mixtures allowed by g.c.-m.s. analysis showed a typical Schulz-Flory distribution of isomers for each C_{3n} fraction ($n > 2$). Chain transfer reactions in metallocene-catalysed polymerization normally occur via β-elimination, which is the main reason for the much lower MW of the products when a comparison with heterogeneous catalysts is made. Although the chain transfer to aluminium has been detected as a minor chain-transfer mechanism, in this case saturated oligomers were totally absent. Both i.r. and ^1H n.m.r. analysis revealed the vinylidenic nature of the terminal double bonds in the collected hydrocarbons mixtures, all these findings being in agreement with an oligomerization mechanism based on β-hydride elimination. The only exception was found in the case of the products of reaction obtained with the $Cp_2^*ZrCl_2$/MAO catalytic system, whose vinyl-terminated short-chained hydrocarbons confirmed a transfer mechanism based on β-methyl elimination[3]. In the presence of hydrogen (propylene/hydrogen = 0.42–3) saturated oligomers can be obtained with slightly lower productivity (463–567 kg mol^{-1} Zr bar^{-1} h^{-1}).

Ethylene/propylene cooligomerization

Considering the low MW obtained with propylene only, the following step was taken with the aim of using the transfer effect promoted by this α-olefin by employing a gaseous mixture composed of ethylene and propylene (C_2/C_3 = 10/90 by weight and about 0.17 by mol). The catalytic systems and the experimental conditions employed were the same as those previously used for propylene oligomerization (*Table 4*). Even in this case, all the products consisted of complex mixtures of olefinic hydrocarbons approximately in the range C_6–C_{30} with a general trend analogous to that observed in the oligomerization of propylene alone. A continuous spectrum with oligomers having odd and even number of carbon atoms showed that effective cooligomerization had taken place through the formation of crossed ethylene–propylene sequences. According to its major reactivity, each oligomeric mixture resulted ethylene-enriched (C_2/C_3 in the range 0.4–1.2 molar) with respect to the gaseous feed, as shown by ^1H n.m.r. integrated areas (*Table 4*). From a comparison of these results with the ones obtained in ethylene homo-oligomerization, one could conclude that the chain transfer reaction is most probably induced by the propylene monomer when the propagating chain end is a propylene unit. Indeed n.m.r. and i.r. analysis indicate the presence of the vinylidenic group as oligomer end groups in the case of $Cp_2Zr(CH_3)_2$ or Ind_2ZrCl_2 (*Scheme 1*) and vinylic groups in the case of the $Cp_2^*ZrCl_2$ complex, thus suggesting a β-CH_3 elimination reaction in the presence of the last catalyst[3].

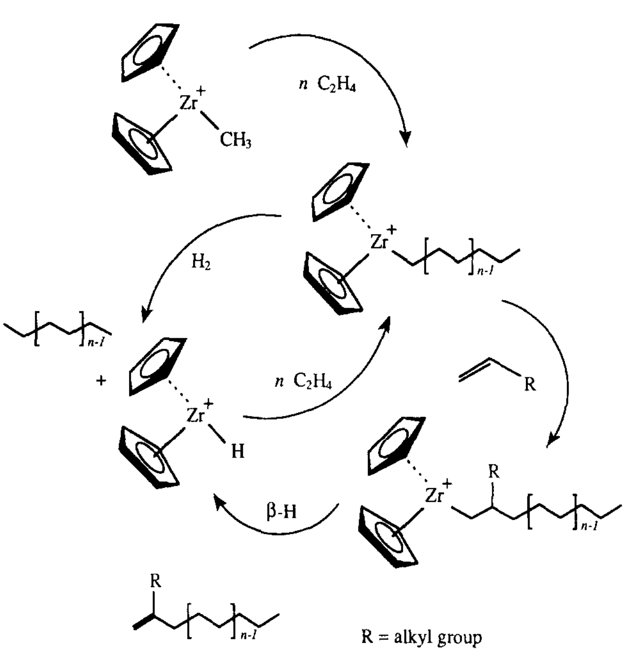
Table 4 Co-oligomerization of a ethylene-propylene mixture using a metallocene and MAO as catalytic system[a]

					Oligomers	
Run	Metallocene	Al/Zr	*T* (°C)	*P* (bar)	Productivity[b]	Range[c]
EP01[c]	Cp_2ZrMe_2	1000	20	1	34	C_6–C_{30+}
EP02[c]	Cp_2ZrMe_2	3000	20	1	83	C_6–C_{30+}
EP03[c]	Cp_2ZrMe_2	3000	20	5	140	C_6–C_{30+}
EP04[c]	Cp_2ZrMe_2	3000	70	1	641	C_6–C_{30+}
EP05	Ind_2ZrCl_2	1000	20	1	100	$>C_{30}$
EP06	Ind_2ZrCl_2	3000	20	1	417	$>C_{30}$
EP07	Ind_2ZrCl_2	3000	20	3	333	$>C_{30}$
EP08	Ind_2ZrCl_2	3000	70	1	783	$>C_{30}$
EP09	$Cp_2^*ZrCl_2$	1000	20	1	183	C_6–C_{24}
EP10	$Cp_2^*ZrCl_2$	3000	20	1	584	C_6–C_{24}
EP11	$Cp_2^*ZrCl_2$	3000	20	5	223	C_6–C_{24}
EP12	$Cp_2^*ZrCl_2$	3000	70	1	700	C_6–C_{18}
EP13	$Cp_2^*ZrCl_2$	3000	70	2	467	C_6–C_{18}

[a] In toluene with 6.0 μmol metallocene, duration 1 h, $C_2/C_3 = 0.17$ by mol

[b] kg PE mol^{-1} Zr h^{-1}

[c] $C_2/C_3 = 1.27$ (run EP01), $C_2/C_3 = 1.22$ (run EP02), $C_2/C_3 = 0.41$ (run EP03), $C_2/C_3 = 0.37$ (run EP04) in the product mixture



Scheme 1 Proposed mechanism for ethylene/α-olefin cooligomerization

Ethylene/α-olefins cooligomerization

On the basis of the above results propylene was replaced with several liquid α-olefins such as 1-hexene (HEX), 4-methyl-1-pentene (4MP) and 1-octene (OCT), with the aim to investigate more thoroughly the comonomer action as a chain transfer agent. Polymerizations were carried out in the presence of the homogeneous system $Cp_2Zr(CH_3)_2$/MAO at two different temperatures (20 and 70°C), molar ratio MAO/Zr 1000 and α-olefin concentration in the range 0.8–3.0 M (*Table 5*). Since the incorporation of a α-olefin into the polymer has been reported to be very low, a constant comonomer concentration was assumed in the copolymerization experiments ($P_{C_2H_4}$ = 1 bar) throughout the reaction[17].

In the absence of ethylene the liquid monomers produced only gas chromatographically detectable

Table 5 Co-polymerization between ethylene and liquid α-olefins using Cp_2ZrMe_2/MAO as catalytic system[a]

	α-Olefin				Polymer[c]		
Run	(type)	c(M)	T (°C)	Oligomers[b] Productivity[d]	Productivity[d]	%[e]	MW[f]
EH00	HEX	2.0	20	135	—	—	—
EH02	HEX	1.4	20	186	3186	49.8	2500
EH03	HEX	2.0	20	544	2576	45.2	2800
EH04	HEX	2.0	70	628	2322	12.1	2400
EH05	HEX	3.0	70	797	2186	3.7	2400
ET00	4MP	2.0	20	85	—	—	—
ET01	4MP	1.4	20	237	1729	33.3	1800
ET02	4MP	2.0	20	493	1678	18.0	2400
ET03	4MP	3.0	20	1231	1746	8.3	2800
EO00	OCT	2.0	20	68	—	—	—
EO01	OCT	1.4	20	204	2407	33.8	2900
EO02	OCT	2.0	20	373	1780	31.0	2800
EO03	OCT	2.0	70	458	1695	11.1	3000
EO04	OCT	3.0	70	865	1542	8.2	7000

[a] In toluene with 1 bar ethylene, 5.9 μmol metallocene, [Al]/[Zr] = 1000, duration 1 h

[b] Soluble oligomeric produces

[c] Toluene insoluble polymer

[d] $kg\,PE\,mol^{-1}\,M\,t\,h^{-1}$

[e] Polymeric fraction insoluble in n-pentane

[f] Mean molecular weight of n-pentane insoluble fraction determined via viscosity measures in decalin at 135°C

products (up to C_{30+}) with productivity decreasing with increasing the steric hindrance of the alkyl group of the α-olefin (see runs EH00, ET00 and E000 in *Table 5*)[12,22].

On the other hand all the copolymerization reactions produced both oligomers in the range C_8–C_{40}, and waxy and sticky polymers in amounts and ratios directly connected to the temperature of reaction and to the α-olefin content. In particular, the weight ratio oligomers/polymer seemed to be affected by increasing both parameters, though the conditions employed did not permit the exclusive formation of oligomers in the C_8–C_{40} range. A major incidence of transfer reactions resulted when 4MP was used, thus suggesting that the side chain branching of the olefin favours the β-H transfer.

The oligomers soluble in the polymerization solvent were investigated by g.c. analysis showing the presence of a mixture of co-oligomers in the C_{10}–C_{40} region.

After removing this fraction, an oily and viscous liquid remained whose components could not be detected via GC-analysis. These polymeric products were successively submitted to extraction with n-pentane, thus resulting in separating a fraction of solid polymer from a wax-like and low-melting one. Viscosimetric determinations of the average MW of the former portion evidenced values well below those of ethylene homopolymers obtained with the same catalytic systems and under the same experimental conditions.

The weight fraction of this last polymer decreases with increasing the liquid α-olefin content and the temperature from 20 to 70°C. I.r. characterization of the hydrocarbon mixtures revealed vinylidenic terminated polymer chains. Therefore, these results can be looked on as if the α-olefin comonomer acts as a termination agent, causing a break in active metal–carbon bonds through the β-H elimination process which is favoured in the case of a tertiary hydrogen atom (*Scheme 1*).

CONCLUSIONS

The data presented in this paper provide further insight about the role of the various chain transfer reactions during the polymerization of 1-alkenes in the presence of nonbridged metallocene catalyst. Significant analogies and differences with respect to more conventional supported catalysts have been observed thus confirming the general similarity between chemical mechanism with the two classes of catalysts.

However, metallocene catalysts show a more evident sensitivity to various parameters thus allowing a more extensive control of molecular weight and the possibility to produce liquid oligomers only, both during homo- or copolymerization (oligomerization) reactions.

The complex systems of successive and parallel reactions cannot be simply rationalized, as individual reactions appear to be affected to a different extent by reaction conditions and monomer structure. However, these data allow the depiction of a schematic mechanism for the reaction occurring with ethylene, which is ideally related to that describing 1-butene dimerization reported by Resconi *et al.*[3]. Indeed, with non-bridged metallocenes ethylene homopolymerization (*Scheme 1*) proceeds to solid polymers even at temperatures around 70–80°C and the use of a certain hydrogen pressure is necessary to obtain liquid products. The presence of an α-olefin, which after insertion in the growing chain preferentially gives β-elimination (H or CH_3), allows the production of oligomers from ethylene even in the absence of hydrogen which are characterized by vinylidenic end groups. The two effects largely overwhelm the chain transfer by the cocatalyst. Indeed, MAO does not give any appreciable MW reduction with increasing concentration and aluminium alkyls become effective at high concentration, thus negatively affecting productivity. More branched oligomers can be expected with bridged metallocene catalysts having a more extensive propagation capacity for α-olefins, even if a lower incidence of transfer reaction can be predicted.

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