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Comparative behaviour of hafnium and titanium catalysts in copolymerization of α-olefins *

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Abstract

Supported hafnium and titanium catalysts were prepared under the same conditions starting from the corresponding tetrakisbutanolates, which were supported on $MgCl_2$ by reaction of a suspension of Hf/Mg catalyst with aluminum alkyl chlorides. The systems were employed in the copolymerization of 1-hexene with 4-methyl-1-pentene. The extent of polymerization, as well as the copolymer composition, sequence distribution, stereoregularity, and molecular weight were evaluated. The hafnium catalysts gave higher molecular weights and better isotactic stereoregularity but displayed lower activity than the titanium catalysts, but the co-monomer distributions were similar for the two systems. These results are discussed in terms of the number and type of active sites.

Introduction

In a preliminary communication [1] it was reported that hafnium catalysts supported on $MgCl_2$ can polymerize propylene and 4-methyl-1-pentene with lower activity but higher stereospecificity than the corresponding Ti-catalysts. As the systems used were prepared strictly by the same procedure as the bimetallic (Hf/Ti) systems utilised for the preparation of various linear low-density polyethylenes (LLDPEs), it seemed of interest to study the homo- and co-polymerization of different 1-alkenes in order to provide more complete information on the behaviour of the two metals during monoalkene polymerization. Thus we carried out an investigation of the copolymerization of a linear α-olefin, 1-hexene (HE), with a branched one, 4-methyl-1-pentene (4MP), in the presence of model catalysts based on hafnium or titanium as the sole transition metal. It was expected that the

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* In memory of Professor Piero Pino.

difference in the steric hindrance provided by the two monomers used would allow identification of significant differences in the copolymerization and homopolymerization carried out in the presence of catalysts having different compositions in respect of the transition metal used (Hf or Ti) and the ratio between the metal and the magnesium chloride (the dilution of the active species on the supporting medium). Such an approach represents a first step in gaining insights into the nature of active sites in the systems studied.

Experimental

Materials

$Al(^iC_4H_9)_3$ was a commercial product (Schering) and used without further purification. 4-Methyl-1-pentene was purified by refluxing over metallic sodium followed by distillation. Research grade n-heptane was purified by the usual procedure. Magnesium-supported hafnium and titanium catalysts were prepared as previously described [2–4].

Polymerization experiments

The same procedures were used for homopolymerizations and copolymerizations. Data for individual runs are summarized in Tables 1–3, and detailed information is given only for the following typical experiments.

Run M31. A solution of 35.0 g (0.42 mol) of 1-hexene in 300 ml of n-heptane was placed in a Schlenk vessel provided with magnetic stirring and 8.0 ml (8.0 mmol) of 1 *M* solution of $Al(^iC_4H_9)_3$ in n-heptane and 7.0 ml (0.84 mmol Hf) of Hf/Mg catalyst suspension in n-heptane were added successively. The mixture was stirred at 25 °C for 5 h, then the polymerization was quenched with acidified methanol and the coagulated polymer was dried under vacuum to yield 10.2 g (29%) of polymeric product.

Table 1

Homopolymerization of 1-hexene in the presence of hafnium catalyst [a]

Run	Mg/Hf (mol/mol)	Al/Hf (mol/mol)	Temp. (°C)	Duration (h)	Conv. [b] (%)	$[\eta]$ [c] (dl/g)	V_p [d]
M31	1.0	10.0	25	5.0	29	7.0	6
M30	7.2	10.0	25	5.0	43	6.3	9
M32	1.0	5.0	25	0.25	4	5.7	16
				0.5	6	6.0	8
				1.0	10	7.9	8
				2.0	16	9.4	6
				5.0	35	10.1	6
M33	1.0	2.5	25	5.0	25	9.1	5
M34	1.0	1.0	25	5.0	16	9.7	3
M39	1.0	5.0	40	5.0	70	6.7	14
M41	1.0	5.0	60	5.0	82	4.7	16

[a] In n-heptane, molar ratio olefin/transition metal (Hf) = 500. [b] Evaluated as (polymer weight/olefin weight)·100. [c] In decahydronaphthalene at 135 °C. [d] Evaluated as percent conversion/h.

Table 2

Copolymerization of HE and 4MP in the presence of Hf catalyst

Run	Experimental conditions [a]		Conv. [b] (%)	Copolymer			
	HE (%-mol)	Duration (h)		$[\eta]$ [c] (dl/g)	HE [d] (%-mol)	l_{4MP} [e]	l_{HE} [e]
M90	25	21	83	6.2	27	4.3	1.7
M11	50	16	85	8.0	48	2.6	2.4
M91	75	21	87	n.d.	77	1.5	4.5
M17	90	20	66	6.2	93	1.4	12.1
M118	25	2	19	9.5	41	2.9	2.1
M122	50	2	21	7.4	66	1.8	3.4
M117	75	2	33	7.5	86	1.4	7.8

[a] In n-heptane at 25 °C, molar ratio comonomers/Hf = 600, molar ratio Hf/Mg = 1, molar ratio $Al(^{i}C_4H_9)_3$/Hf = 30. [b] Evaluated as (polymer weight/comonomers weight) · 100. [c] In decahydronaphthalene at 135 °C. [d] Evaluated by ^{13}C NMR. [e] Mean sequence length, evaluated by ^{13}C NMR.

Table 3

Copolymerization of HE and 4MP in the presence of Ti catalyst

Run	Experimental conditions [a]		Conv. [b] (%)	Copolymer			
	HE (%-mol)	Duration (h)		$[\eta]$ [c] (dl/g)	HE [d] (%-mol)	l_{4MP} [e]	l_{HE} [e]
M94	25	20	99	2.5	25	5.7	1.8
M93	50	20	99	2.1	50	2.9	2.7
M95	75	20	95	2.0	75	1.7	4.6
M127	25	0.1	18	3.8	37	3.6	2.0
M128	50	0.2	24	2.4	65	2.1	3.5
M129	75	0.2	17	2.9	83	1.7	8.0
M116 [f]	50	18	57	7.5	63	2.3	3.7

[a] In n-heptane at 25 °C, molar ratio comonomers/Ti = 1800, molar ratio Ti/Mg = 1, molar ratio $Al(^{i}C_4H_9)_3$/Ti = 30. [b] Evaluated as (polymer weight/comonomers weight)·100. [c] In decahydronaphthalene at 135 °C. [d] Evaluated by ^{13}C NMR. [e] Mean sequence length, evaluated by ^{13}C NMR. [f] Run carried out in the presence $TiCl_3/Al(C_2H_5)_2Cl$, molar ratio comonomers/Mt = 100, Al/Mt = 1.5.

Run M32. A solution of 35.0 g (0.42 mol) of 1-hexene in 300 ml of n-heptane was placed in a Schlenk vessel provided with magnetic stirring and 4.0 ml (4.0 mmol) of 1 *M* solution of $Al(^{i}C_4H_9)_3$ in n-heptane and 7.0 ml (0.84 mmol Hf) of Hf/Mg catalyst suspension in n-heptane were added successively. The mixture was stirred at 25 °C. At intervals small samples of the slurry were removed, coagulated with acidified methanol, dried under vacuum, and weighed. After 5 h, the polymerization was quenched with acidified methanol and the coagulated polymer was dried under vacuum to yield 12.3 g (35%) of polymeric product.

Run M127. A solution of 2.5 g (30 mmol) of 1-hexene and 7.5 g (90 mmol) of 4-methyl-1-pentene in 40 ml of n-heptane was placed in a Schlenk vessel provided with magnetic stirring and 2.0 ml (2.0 mmol) of 1 *M* solution of $Al(^{i}C_4H_9)_3$ in n-heptane, and 1.5 ml (0.066 mmol Ti) of Ti/Mg catalyst suspension in n-heptane were added successively. The mixture was stirred at 25 °C for 0.1 h, then the polymerization was quenched with acidified methanol and the coagulated polymer was dried under vacuum to yield 1.8 g (18%) of polymeric product.

Polymer characterization

NMR spectra were recorded on a Varian Gemini 200 spectrometer in 5 mm tubes with 10% (w/v) solutions in 1,2,4-trichlorobenzene at 110 °C. ^{1}H NMR spectra were recorded at 200 MHz. Spectral conditions were as follows: size, 11,968 points; spectral width, 3 kHz; pulse, 30 °; acquisition time, 2 s; number of scans, 1. ^{13}C NMR spectra were recorded at 50.3 MHz, under conditions of full proton decoupling. Spectral conditions were as follows: size, 23936 points; spectral width, 15 kHz; pulse, 70 °; relaxation delay, 2 s; acquisition time, 0.8 s; number of scans, 20000. No weighing function was applied before the Fourier transformation.

Viscosity measurements were carried out in tetrahydronaphthalene at 135 °C with a Desreaux–Bischoff dilution viscometer. IR spectra were recorded on polymer films on a Perkin–Elmer 1600 FT-IR spectrophotometer; the D_{996}/D_{918} ratios were evaluated from the integrated absorbances of the 918 and 996 cm^{-1} bands. Differential scanning calorimetry (DSC) analyses were performed in the 50–300 °C range on 5–10 mg polymer samples with a Mettler TA 4000 calorimeter. The melting point was taken to be the onset of the melting transition at 10 °C/min heating and cooling rates.

Results and discussion

Homopolymerization of 1-hexene (HE)

The homopolymerization of 1-hexene (HE) was carried out in the presence of hafnium catalysts supported on $MgCl_2$, with variation in the Mg/Hf and Al/Hf ratios and the reaction temperature (Table 1). The polymerization rate does not appreciably change upon dilution of hafnium in the $MgCl_2$ support (Runs M31 and M30). In contrast, a definite increase is observed when the Al/Hf ratio is increased from 1 ($V_p = 3$) to 10 ($V_p = 6$), or the temperature from 25 °C ($V_p = 6$) to 60 °C ($V_p = 16$). Over the same temperature range, however, the polymer viscosity decreases from 10 to 5 dl/g, at a constant Al/Hf or Mg/Hf ratio. A significant

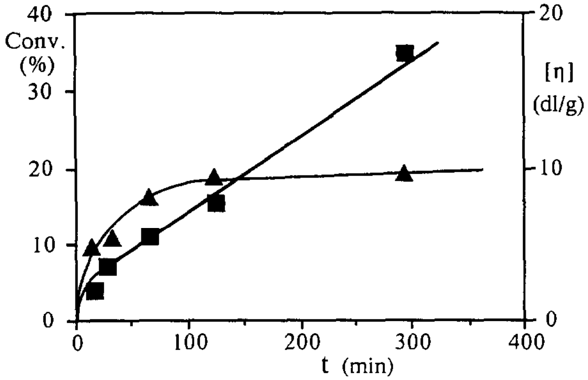

Fig. 1. Time dependence of conversion (-■-) and intrinsic viscosity (-▲-) in the homopolymerization of HE in the presence of $Hf/MgCl_2$ catalyst.

reduction of polymer molecular weight is also observed at high Al/Hf molar ratios. In the reaction at 25° C (Mg/Hf = 1, Al/Hf = 5.0), after an induction period of about 25 min, the polymer yield appears to linearly increase at least up to 35% conversion, suggesting that in this range the polymerization rate (after the induction period) is substantially constant or decreases smoothly. Indeed the moderate decrease in rate with time could be related to the decrease of monomer concentration. The molecular weight, as monitored by viscosity, increases in the first 100 min, and

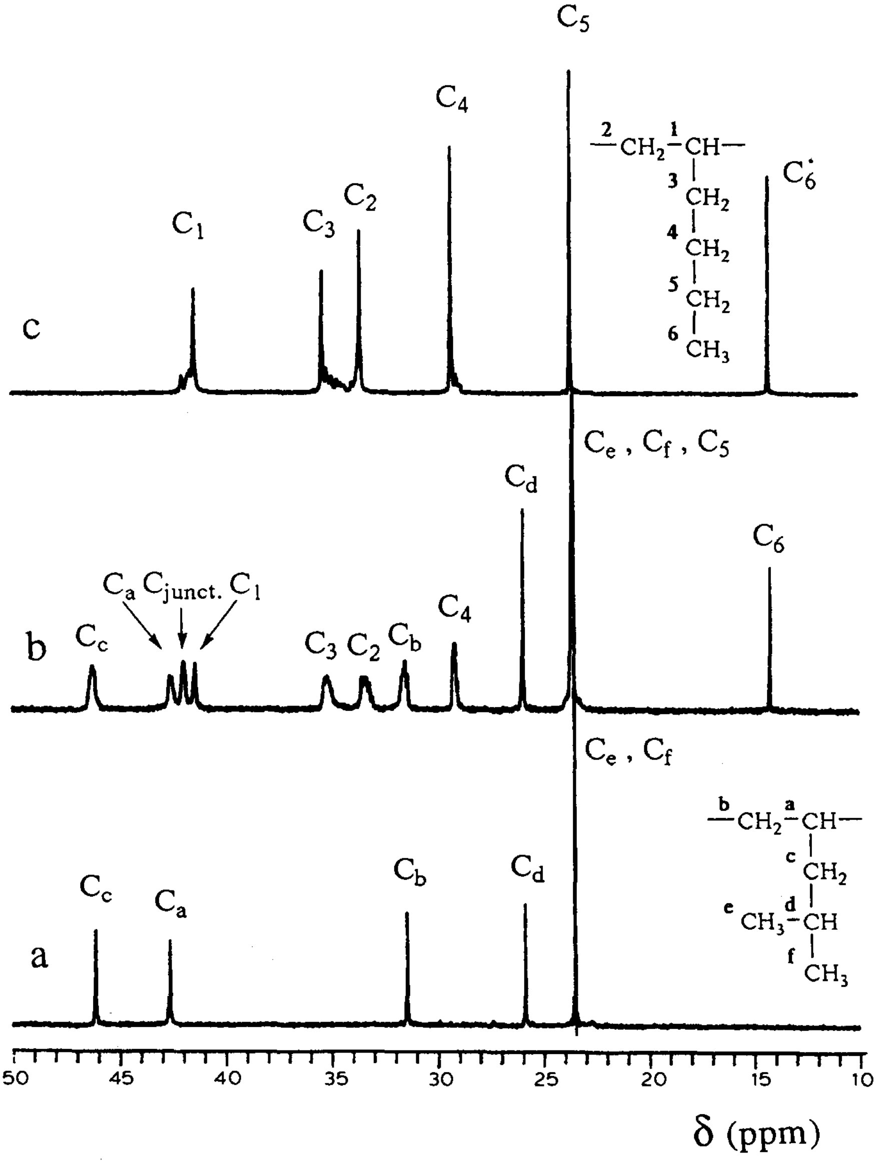

Fig. 2. ^{13}C NMR spectra and peak assignments of (a) poly(4MP) (Sample M188), (b) poly(4MP-co-HE) containing 48%-mol of 4MP units (Sample M11), and (c) poly(HE) (Sample M30) obtained in the presence of Hf/Mg catalyst.

then tends towards a limiting value (Fig. 1). As the polymerization was carried out in the absence of hydrogen, transfer reactions must be therefore involved; these are probably more effective with 1-alkenes than with ethylene [3], owing to both the lower propagation rate and the presence in the last inserted unit of a tertiary hydrogen atom β to the transition metal. The large decrease in viscosity resulting from an increase in the Al/Hf molar ratio suggests that AlR_3 plays an important role in the transfer.

In any case the molecular weight attained in the presence of Hf is higher than that with Ti, in spite of the higher activity of the latter. These results are consistent with those reported previously for the homopolymerization of 4-methyl-1-pentene (4MP) [2]. Under similar conditions the intrinsic viscosity obtained with Ti was 2.4 dl/g compared with 7.0 gl/g (Run M30).

The ^{13}C NMR spectrum of unfractionated poly(HE) exhibits six main resonances flanked by minor peaks (Fig. 2). Up to now no conclusive stereochemical assignment of these signals has been made, but the major peaks must be attributed to rather long isotactic sequences and the smaller ones to less regular stereosequences [5]. Their relative intensity demonstrates that all the prepared samples are characterized by a high degree of isotacticity, despite the fact that the poly(1-hexene) is amorphous at room temperature. The content of long isotactic sequences is definitely higher in polymers formed in the presence of Hf catalysts ($\approx 90\%$) than in those obtained with Ti catalysts ($\approx 85\%$). Similar indications were obtained by solvent extraction [1] and from the ^{13}C NMR spectra of poly(4MP) [2].

Copolymerization of HE with 4MP

Several copolymerization experiments were carried out in the presence of Hf (Table 2) and Ti (Table 3) catalysts starting with monomer mixtures of various compositions (HE/4MP 0.33 to 9.0). In some cases polymerizations were interrupted at a relatively low conversion ($< 35\%$) in order to ensure reasonable homogeneity of the macromolecules in respect of composition and monomer sequence distribution. Owing to severe peak overlapping, the copolymer composition can not be very easily assessed by ^{1}H NMR spectroscopy. With sufficient relaxation delay between transients, more reliable results are obtained from the relative intensities of ^{13}C NMR side chain methylene signals. As expected from the lower steric hindrance of the linear side chain of HE with respect to the branched isobutyl group of 4MP, in all the experiments the copolymers resulted enriched in the former monomer with respect to the polymerization feed. Moreover this HE enrichment is more substantial with Hf, which therefore seems to be more sensitive to steric hindrance than Ti, in accordance with its higher stereospecificity [1].

Detailed indications about the microstructure of the macromolecules can be derived from ^{13}C NMR data in respect of main-chain stereochemistry and monomer sequence distribution. The ^{13}C NMR spectrum of 4MP/HE copolymer samples (Fig. 2) shows a set of resonances almost coincident with those present in the spectra of the two corresponding homopolymers.

In addition to signals present in the spectra of homopolymers, a new peak is observed at about 42 ppm, between the signals at 41.4 and 42.5 ppm that were assigned to main chain methylene of sequences of HE and 4MP units, respectively (Fig. 3). The 42 ppm resonance, whose relative intensity definitely depends on the copolymer chemical composition, must be attributed to main chain methylene

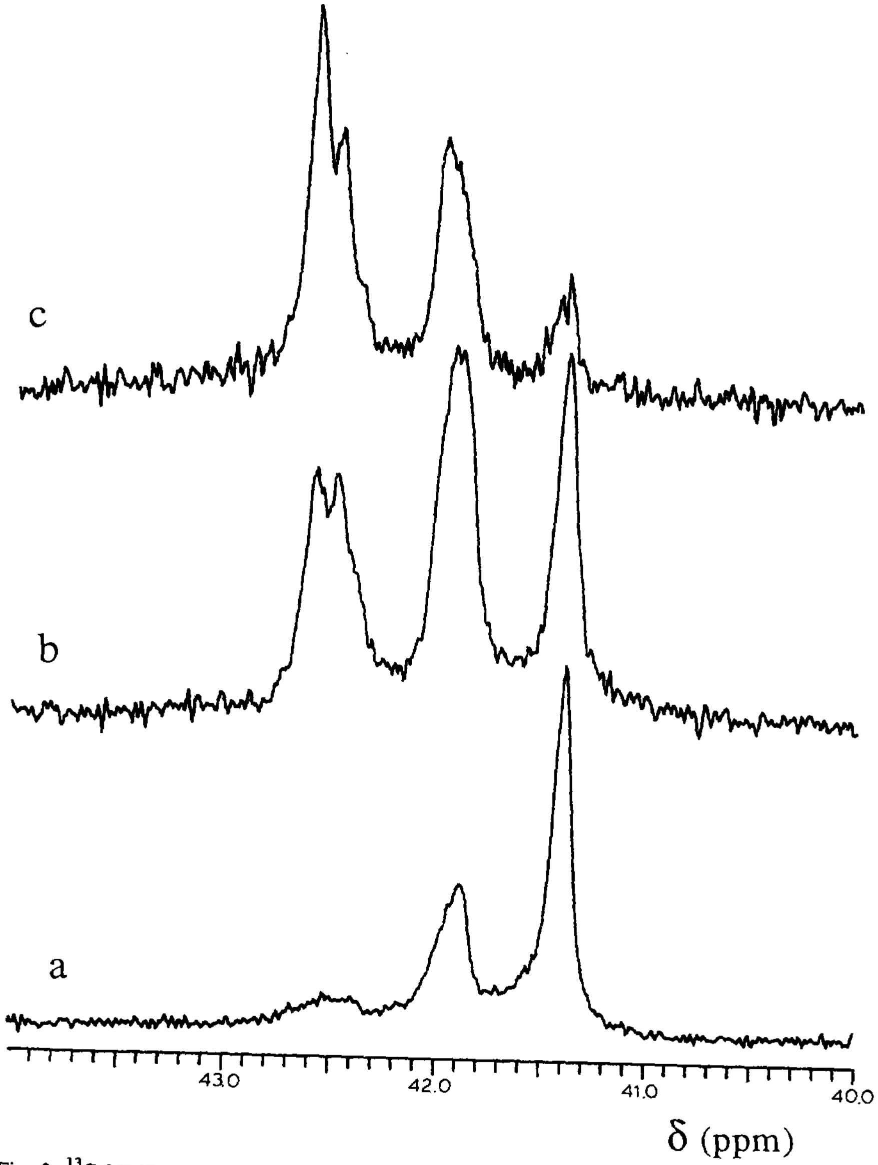

Fig. 3. ^{13}C NMR spectra in the 40–44 ppm region of poly(4MP-co-HE) obtained in the presence of Hf/Mg catalyst and containing (a) 77% (Sample M90), (b) 48% (Sample M11), and (c) 27% (Sample M91) of HE units.

carbons included between one HE and one 4MP unit (junctions). From the relative intensities of these three methylene signals and within the limits of experimental errors (mainly due to partial signal overlap) it is possible to evaluate the HE and 4MP mean sequence lengths in the various copolymer samples [6]. The values reported in Tables 2 and 3 indicate that the investigated catalysts give rise to copolymer macromolecules having a quasi-random distribution of the monomeric units, with some tendency to form slightly longer HE sequences due to the higher

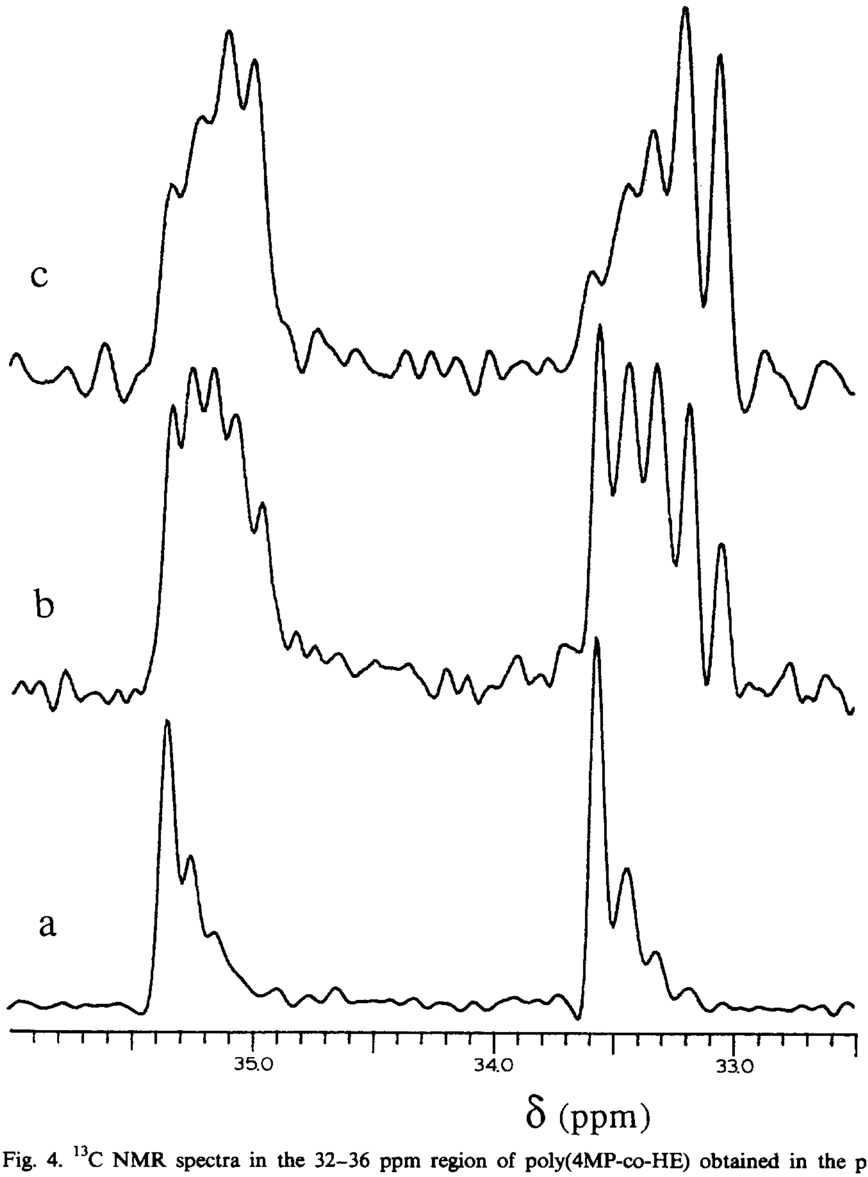

Fig. 4. ^{13}C NMR spectra in the 32–36 ppm region of poly(4MP-co-HE) obtained in the presence of Hf/Mg catalyst and containing (a) 77% (Sample M90), (b) 48% (Sample M11), and (c) 27% (Sample M91) of HE units. A resolution enhancement function ($e^{t/RE}e^{-t/AF}$, RE = 0.15 s, AF = 0.3 s) was applied to the free induction decay (FID) before the Fourier transformation (FT).

reactivity of this monomer with both metals. Close inspection of the ^{13}C NMR spectra also reveals that signals at about 28, 31, 33, 35, and 46 ppm are split into five components (Fig. 4); since their relative intensities depend on the copolymer chemical composition, these splittings can be attributed to sequences of different monomeric units (pentads). However, ten resonances are expected for pentads and therefore this assignment remains tentative.

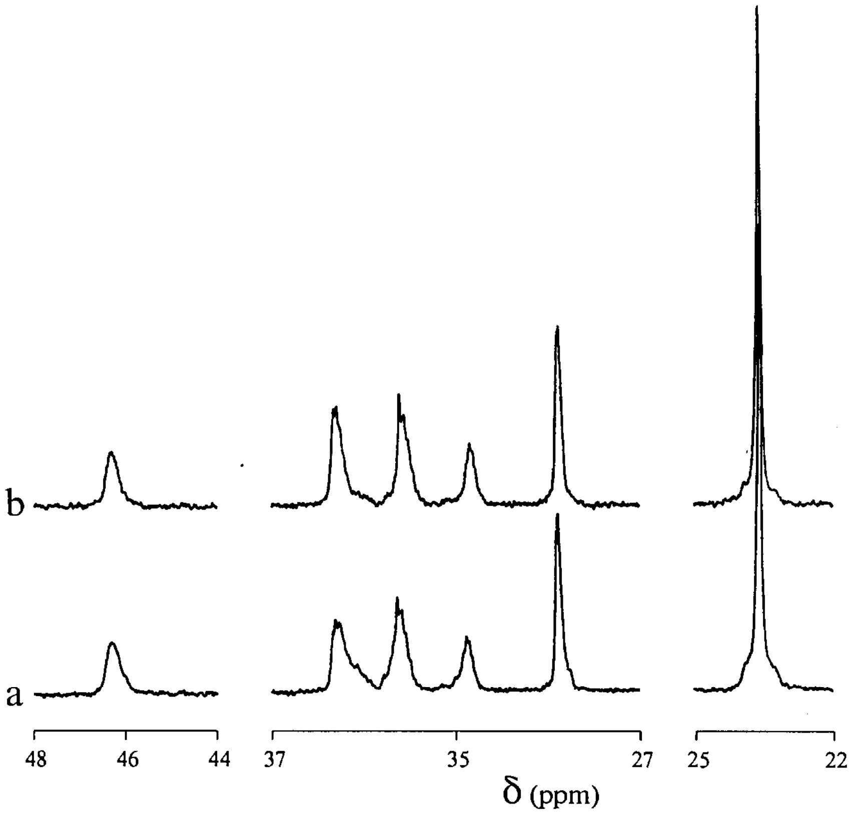

Fig. 5. ^{13}C NMR signals of C_c (48–44 ppm), C_3, C_2, C_b, C_4 (37–27 ppm), and C_e, C_f, C_5 (25–22 ppm) carbon atoms of poly(4MP-co-HE) samples containing about 35%-mol of HE units, obtained in the presence of (a) Ti/Mg catalyst (Sample M128) and (b) Hf/Mg catalyst (Sample M122).

The spectra also provide some indication of the copolymer tacticity. Indeed, apart from the previously discussed modification of signals due to copolymer composition, the small signals flanking the major resonances have positions and relative intensities very close to those for the corresponding homopolymers. These signals have been related to the tacticity of homopolymer chains, and it thus seems very likely that the copolymer macromolecules have a predominantly coisotactic structure. On this basis, copolymer samples prepared in the presence of the Hf catalyst appear to be slightly more isotactic than the corresponding samples obtained with the Ti catalyst (Fig. 5).

The number of 4MP units inserted in sequences can be evaluated either by ^{13}C NMR, from the intensities of the peaks at 42.5 and 41.9 ppm, or by IR spectroscopy [7] from the ratio of the integrated absorbances of the bands at 996 and 918 cm^{-1} (Table 4). Values obtained from the NMR data correspond to 4MP sequences of two or more units and are larger than those obtained from the IR spectra. This apparent discrepancy can be explained by taking into account the previous attribution of the 996 cm^{-1} band to helical polymer segments constituted by four or more 4MP units [7].

Table 4

Characterization of HE/4MP copolymers

Sample	4MP (%-mol)	D_{996}/D_{918}	4MP units in sequence		T_m (°C)
			by IR[a] (%-mol)	by ^{13}C NMR[b] (%-mol)	
ME24	100	0.77	100	100	225
M118	59	0.38	49	64	137
M122	34	0.19	25	43	110
M117	14	0.01	1	35	85
M127	63	0.37	48	74	127
M128	35	0.18	23	56	108
M129	17	0.01	1	43	93
M116	37	0.19	25	60	153

[a] Evaluated from D_{996}/D_{918} relative to poly(4MP). [b] Evaluated as $100 \cdot I_{40.5\ \mathrm{ppm}}/(I_{40.5\ \mathrm{ppm}} + 0.5 \cdot I_{40\ \mathrm{ppm}})$.

The spectroscopic data strongly indicate that, with minor variations, copolymers prepared in the presence of the investigated supported systems or with a more conventional Ziegler–Natta catalyst [$TiCl_3/Al(C_2H_5)_2Cl$] have a substantially random distribution of monomeric co-units. Analogous indications (Table 4) are provided by the monotonic decrease of the melting temperature (T_m) with increases in the content of HE units [8].

Conclusions

Catalysts prepared by coprecipitation of hafnium and magnesium chlorides, when activated with aluminum alkyls can bring about homopolymerization α-olefins (in particular 1-hexene) to high molecular weight species. The molecular weight increases with the extent of conversion (and time) up to about 15–20% conversion. Later the molecular weight tends towards a limiting value, indicating that transfer reactions become more efficient than with ethylene [9]. However, this limiting value is higher than that obtained under the same experimental conditions in the presence of analogous titanium catalysts.

This trend is confirmed in the copolymerization of 1-hexene with 4-methyl-1-pentene, where the Hf-catalyst gives lower polymerization rate than the titanium-catalyst but a higher molecular weight and isotactic stereoregularity for both co-units. However, a more detailed analysis of the copolymerization products indicates that the copolymer composition and the substantially random sequence distribution are similar in the two cases.

This feature leads to the suggestion that the active sites for α-olefins homo- and co-polymerization are similar in the two systems. This conclusion is not in conflict with the observation that different isotacticity and molecular weight are obtained in the presence of Hf and Ti catalysts; the higher degree of polymerization obtained with Hf can be explained in terms of the higher stability of the Hf–C σ-bond to transfer reactions [10] without influence on the copolymer sequence distribution. Some effect on the sequence distribution could be expected in view of the larger sensitivity to the steric hindrance of the hafnium catalyst, as shown by the better isotactic control, which may also be responsible for its lower activity with respect to the titanium-catalyst. However, the difference in activity is much larger than that in stereospecificity, supporting the view that a smaller fraction of Hf atoms participate in the polymerization process; at present this can be only tentatively accounted for by assuming that the steric effect is reduced during the cross-copolymerization reactions, but more detailed experiments with comonomers showing larger differences in steric hindrance are necessary before a final conclusion can be reached.

Acknowledgements

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References

1 F. Masi, F. Menconi, S. Malquori, N. Zandonà, A. Altomare and F. Ciardelli, Makromol. Chem., Rapid Commun., 10 (1989) 485.
2 F. Masi, S. Malquori, L. Barazzoni, C. Ferrero, A. Moalli, F. Menconi, R. Invernizzi, N. Zandonà, A. Altomare and F. Ciardelli, Makromol. Chem., Suppl., 15 (1989) 147.
3 F. Masi, S. Malquori, L. Barazzoni, R. Invernizzi, A. Altomare and F. Ciardelli, J. Mol. Catal., 56 (1989) 143.
4 F. Ciardelli, F. Masi, S. Malquori, C. Ferrero, L. Barazzoni, F. Menconi, A. Moalli and R. Invernizzi, (Enichem Anic) Italian Patent 22115A/88 (1988).
5 Y. Nishiyama and T. Asakura, Polym. Prepr. Jpn., 36 (1987) 2408.
6 J.C. Randall, Polymer sequence determination Carbon-13 NMR method. Academic Press, New York, 1977.
7 N.G. Bakayutov, Yu.V. Kissin, I.I. Vavilova, Z.V. Arkhipova and B.V. Yerofeyev, Vysokomol. Soyed., Ser., A, 17 (1975) 2163.
8 A. Turner Jones, Polymer, 6 (1969) 549.
9 N. Zandonà and F. Ciardelli, Polymer, 32 (1991) 1131.
10 D.J. Cardin, M.F. Lappert and C.L. Raston, Chemistry of Organo-Zirconium and -Hafnium Compounds, Ellis Horwood, London, 1985.