

Zeolite supported polymerization catalysts: Copolymerization of ethylene and α -olefins with metallocenes supported on HY zeolite

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Abstract

Copolymerization of ethylene with higher α -olefins, such as 4-methyl-1-pentene, 1-hexene, 1-octene and 1-dodecene, was carried out with both aspecific and isospecific bridged metallocene complexes, comparing the catalytic behaviour following metallocene supportation on methylalumoxane-pretreated HY zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.7$). A decrease in specific activity was generally observed after adsorption on zeolite of both non bridged and *ansa*-metallocene complexes, though molecular weights of the copolymers were found to be higher especially when employing α -olefins as polymerization solvents. On the other side, the incorporation of the α -olefin comonomer was reduced in the case of supported biscyclopentadienylzirconium dichloride, whereas similar contents of olefin units were incorporated in the copolymers prepared with soluble or supported *ansa*-zircono- or hafnocene. NMR analysis and DSC determined melting points of the produced copolymers are connected with a shape selectivity effect promoted by the support. © 1998 Elsevier Science B.V.

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1. Introduction

Despite the great advantages gained by the advent of homogeneous metallocene catalysts for olefin polymerization and copolymerization, when compared to Ziegler conventional catalysts [1–3], the former complexes have to be heterogenized for the use in many industrial processes and for obtaining uniform polymer particles and high bulk density. A number of studies then appeared in the last few years on

the immobilization of different kinds of metallocenes on inorganic carriers, such as silica, alumina, MgCl_2 and other metal oxides, which are characterized by amorphous structures and broad pore size distribution [4–11]. These catalysts were in a few cases proved to be able to polymerize α -olefins with activities comparable to those of the homogeneous ones but in general an improvement of the physical properties of the produced polymers was obtained.

On the other side, HY zeolites are well known for their crystalline structures, defined narrow pore size distribution and large surface area [12]. Previous studies in this context showed that these materials are suitable supports be-

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cause of the possibility of entrapping in the pores organometallic complexes [13,14]. Biscyclopentadienyl dichloro or dimethyl zirconium were supported on modified HY zeolites to give catalysts showing the same activity as the homogeneous analogs but higher stability during polymerization reactions [15]. Indeed, it was recently reported that NaY zeolite-entrapped metallocenes, obtained by supporting Cp_2ZrCl_2 and Cp_2TiCl_2 ($\text{Cp} = \eta^5\text{-cyclopentadienyl}$) onto MAO-pretreated NaY, afforded ethylene polymerization with a small amount of additional MAO [16].

Different activity and cocatalyst sensitivity could be associated to a field effect by the zeolite and/or catalytic complex structural modification during supportation. Copolymerization experiments can be rather informative in this connection. Indeed silica- or alumina-supported metallocenes, activated by trialkylaluminum compounds, resulted in giving random copolymers whose molecular weights were much higher than those obtained with homogeneous catalysts. Furthermore, the polymer yield markedly increased with increasing comonomer concentration in the feed [17]. A number of ^{13}C -NMR studies showed that the composition is strongly dependent on the catalytic system, namely the transition metal and the ligand structure [18,19].

In this paper some results are reported concerning supportation on HY zeolites and their catalytic performance in ethylene copolymerization with α -olefins of aspecific biscyclopentadienyl and bisindenyl complexes as well as bridged isospecific ethylene-bisindenyl complexes. The support effects are compared to what observed operating in homogeneous phase in order to evidence the role of the zeolite in affecting the polymerization process.

2. Experimental part

All operations were carried out under dry argon atmosphere.

Degussa Co. (Germany) HY zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.7$) was dehydrated at 625°C for 12 h prior its use. Polymerization grade ethylene was obtained from Rivoira and used as received. Toluene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-dodecene (Aldrich) were purified by distillation over sodium/potassium alloy. Methylaluminoxane (MAO) (Witco, 30% w/w toluene solution) and Cp_2ZrCl_2 (Janssen) were commercially obtained and used without further purification. $\text{Ind}_2\text{ZrCl}_2$, $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ and $\text{Et}(\text{Ind})_2\text{HfCl}_2$ were prepared according to literature [20–22].

All the supported catalysts were prepared according to the following typical procedure. 9 mmol of MAO (4.5 M in toluene solution) were added to 4.5 g of HY zeolite in 40 ml of toluene. The mixture was vigorously stirred at room temperature for 24 h, then the solid part was washed more than 5 times with 40 ml of toluene. 0.40 mmol of Cp_2ZrCl_2 (0.005 M in toluene solution) were successively added to the suspension of the HY-MAO precursor, followed by stirring the mixture at 60°C for 24 h. The solid part was then washed with toluene and the washing solutions analysed by UV–visible spectrophotometry in order to determine the amount of unadsorbed metallocene present, by subtracting this value from the total amount originally introduced.

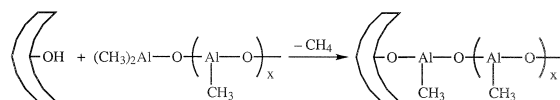
All polymerization experiments were carried out in a 200 ml glass reaction vessel (Büchi) equipped with a mechanical stirrer and a temperature controller with 80 ml of a toluenic solution of the α -olefin or 80 ml of the α -olefin. The liquid comonomer, MAO and the catalyst solution or slurry were transferred in this order under positive pressure of argon. The reaction mixtures were degassed and then ethylene was introduced until the desired pressure was reached. The polymerization experiments were quenched by addition of a 5 vol % HCl/methanol solution and the polymeric products were recovered by filtration, adequately washed with methanol and dried in vacuo at 50°C until constant weight. Specific reaction

conditions may be found in the appropriate tables and in the text.

Molecular weights of the produced copolymers were determined by intrinsic viscosity measurements in decahydronaphthalene (decalin) at 135°C using an Cannon-Fenske viscometer by a one-point method [23] and calculated accordingly [24]. In the case of low molecular weight products, this parameter was estimated by ¹H-NMR analysis. The melting points were measured by differential scanning calorimetric analysis (DSC) on samples which had been previously melted and then recrystallized using a Mettler TA 3000 calorimeter with a heating rate of 15 K/min. The composition of copolymers was determined by ¹H-NMR and ¹³C-NMR analysis at 120°C with a Varian 200 spectrometer. The polymers were dissolved in 1,2,4-trichlorobenzene/benzene-*d*₆ (vol. ratio 9/1) up to 10 wt%. Polymer fractionations were carried out by using Kumagawa-type extractors employing in the order boiling acetone, ethyl acetate, diethyl ether, cyclohexane and toluene.

3. Results and discussion

In order to get a global view of the influence of a HY zeolite support on the catalytic performance of a metallocene complex and on the properties of the resulting copolymers, Cp₂ZrCl₂, Ind₂ZrCl₂, Et(Ind)₂ZrCl₂ and Et(Ind)₂HfCl₂ (Cp = η⁵-cyclopentadienyl, Ind = η⁵-indenyl, Et = 1,2-ethanediyl) were employed as catalyst precursors. Previous experiments demonstrated that the preliminary treatment of the support with MAO is necessary, because of the too many hydroxyl groups on the surface, which cause the displacement of the organic ligand. Taking into account these considerations, each supported catalyst was prepared by adsorption from toluene solution of the metallocene complexes on MAO-pretreated zeolite (Scheme 1). The used HY zeolite was characterized by SiO₂/Al₂O₃ molar ratio = 5.7. All



Scheme 1. Schematic representation of the modification of the zeolite surface with MAO.

the supported catalysts were tested in ethylene/1-hexene copolymerization, comparing their performance with that of the same complexes in solution. The reactions were carried out at 20°C, with Al/Mt (Mt = transition metal) molar ratio = 2 000, ethylene pressure 5 bar and a 1.0 M toluene solution of 1-hexene (Table 1).

Though in the course of the copolymerization experiments quite different effects characterized supported aspecific and stereorigid complexes, a decrease of the catalytic activity was generally observed. As the pretreatment of the support should avoid catalyst decomposition [4,16], this decrease is probably due to the difficult access of the comonomer to the active centers. The copolymers obtained with supported catalysts exhibit a higher molecular weight regardless of the type of metallocene, thus indicating a minor incidence of the chain transfer to comonomer or β-hydride elimination, compared to what observed operating in solution. According to what previously published, bridged hafnium derivatives in solution afforded higher molecular weights and a quite similar trend was observed operating in the presence of the supported systems, thus indicating a substantial maintenance of the original metallocene nature following zeolite supportation [25].

Both DSC and ¹H-NMR spectroscopy analysis gave evidence of a peculiar difference in the composition of the reaction products, which was dependent on the type of metallocene. While a minor concentration of 1-hexene resulted in the copolymers obtained with supported biscyclopentadienyl derivatives compared to what observed in homogeneous phase, no compositional difference was noticed in the case of the stereorigid complexes. This was much more

Table 1

Ethylene/1-hexene copolymerization with metallocene complexes in solution or supported on HY zeolite^a

Run	Catalyst	S.A. (kg/mol Zr · bar · h)	\bar{M}_v ^b	T_m ^c (°C)	C ₆ in copolymer (mol%) ^d
CZ1	Cp ₂ ZrCl ₂	652	7 000	89.4, 116.8	20
CZ2	HY-MAO-Cp ₂ ZrCl ₂	228	63 000	112.0	8
CZ3	Ind ₂ ZrCl ₂	450	21 000	120.0	4
CZ4	HY-MAO-Ind ₂ ZrCl ₂	196	40 000	122.8	< 1
CZ5	Et(Ind) ₂ ZrCl ₂	468	15 000	125.1	36
CZ6	HY-MAO-Et(Ind) ₂ ZrCl ₂	278	22 000	119.7	36
CH1	Et(Ind) ₂ HfCl ₂	36	81 000	94.6, 128.3	16
CH2	HY-MAO-Et(Ind) ₂ HfCl ₂	17	132 000	94.7, 125.5	16

^aReaction carried out at 20°C in 80 ml of 1.0 M 1-hexene solution in toluene, with 5 μmol of Mt in solution or 10 μmol of supported Mt (Mt = Zr or Hf), cocatalyst MAO, [Al]/[Mt] = 2000, ethylene pressure 5 bars, polymerization time 60 min.

^bDetermined by viscosity measurements in decalin at 135°C.

^cMelting point of the copolymer.

^dDetermined by ¹H-NMR analysis.

evident in the case of Cp₂ZrCl₂, whose supportation brought about a marked decrease in the comonomer percentage of the produced polymer (runs CZ1 and CZ2). In this last case the disappearance of one of the two melting points observed with the solution product could be the consequence of a different compositional homogeneity, connected to a lower content of 1-hexene.

This different behaviour could be the consequence of the physical dimensions of two types of complexes, the less crowded biscyclopentadienyl derivatives being able to reach the inner cavities of the zeolite where no access is probably possible for the bridged bisindenyl ones. The active sites in the former case could then own a major discriminating power towards the

two comonomers, leading to a lower 1-hexene incorporation in the macromolecular chains. On the contrary the prevalent surface immobilization of the stereorigid complexes could enable them to maintain the same reactivity ratios as in solution with less marked influence on activity and molecular weight.

The fractionation with boiling solvents was carried out of poly(ethylene-co-1-hexene) samples obtained in the presence of homogeneous and zeolite-supported Cp₂ZrCl₂ in order to evidence the presence of differently structured macromolecules; acetone, ethyl acetate, diethyl ether, cyclohexane and toluene were used in that order (Table 2). Whereas the homogeneous phase produced copolymer (run CZ1) resulted up to 65% soluble in low boiling solvents giv-

Table 2

Characterization of the fractions of poly(ethylene-co-1-hexene) samples obtained with Cp₂ZrCl₂ in solution or supported on HY zeolite

Fraction extracted with	Run CZ1				Run CZ2			
	%	% C ₆ ^a	\bar{M}_v ^b	T_m ^c	%	% C ₆ ^a	\bar{M}_v ^b	T_m ^c
Acetone	39	34	800	—	8	32	600	—
Ethyl acetate	20	26	2 500	83	2	20	3 100	—
Diethyl ether	5	15	6 000	97	0	—	—	—
Cyclohexane	30	6	13 000	116	81	6	65 000	110
Toluene	6	< 1	38 000	122	9	4	93 000	112

^aMolar fraction determined by ¹H-NMR analysis.

^bDetermined by viscosity measurements in decalin at 135°C.

^cMelting point of the polymer fraction in °C.

Table 3

Ethylene/ α -olefins copolymerization with Cp_2ZrCl_2 in solution or supported on HY zeolite^a

Run	α -Olefin	Support	S.A. (kg/mol Zr · bar · h)	\bar{M}_v ^b	T_m ^c (°C)	α -Olefin in copolymer (mol %) ^d
CZ1	HEX	—	652	7 000	89.4, 116.8	20
CZ2	HEX	HY-MAO	228	63 000	112.0	8
CZ7	4MP	—	1,160	3 000	101.3 116.2	8
CZ8	4MP	HY-MAO	270	25 000	119.5	2
CZ9	OCT	—	616	9 000	104.2 120.3	16
CZ10	OCT	HY-MAO	218	59 000	111.7	7
CZ11	DOD	—	578	10 000	107.0 121.6	13
CZ12	DOD	HY-MAO	196	68 000	113.2	5

^aReaction carried out at 20°C in 1.0 M α -olefin (HEX = 1-hexene, 4MP = 4-methyl-1-pentene, OCT = 1-octene, DOD = 1-dodecene) solution in toluene, with 5 μmol of Zr in solution or 10 μmol of supported Zr, cocatalyst MAO, $[\text{Al}]/[\text{Zr}] = 2,000$, ethylene pressure 5 bar, polymerization time 60 min.

^bDetermined by viscosity measurements in decalin at 135°C.

^cMelting point of the copolymer.

^dDetermined by ¹H-NMR analysis.

ing fractions with low molecular weight and high degree of branching, 90% of the product obtained in the supported phase (run CZ2) was extractable only with cyclohexane and toluene, according to the major length and linearity of the polymer chains. These data also confirm the strict correlation between decrease in molecular weight and incorporation of α -olefin.

The effect on catalytic behaviour exerted by the impregnation on zeolite was furtherly confirmed in case of Cp_2ZrCl_2 copolymerization experiments of ethylene with several α -olefins having different linear chain length, such as 1-hexene (HEX), 1-octene (OCT) and 1-dode-

cene (DOD) or with a branched side chain such as 4-methyl-1-pentene (4MP). In all cases the supported catalyst gave lower activity, lower incorporation of α -olefin, higher molecular weight and a single melting temperature (Table 3). The difference particularly in activity and α -olefin content were the largest for 4MP. It is also of interest to note that all the above features showed the same qualitative dependence on comonomer structure in case of both supported and homogeneous catalyst.

The supported zirconocene presented an increase in activity and a reduction of copolymer molecular weight when increasing the initial

Table 4

Ethylene/1-octene copolymerization with Cp_2ZrCl_2 supported on HY zeolite^a

Run	[1-octene] (mol/l)	S.A. (kg/mol Zr · bar · h)	C_8 in copolymer (mol %) ^b	\bar{M}_v ^c	T_m ^d (°C)
CO0	—	313	—	352 000	140.2
CO1	0.2	589	3.5	126 000	113.8
CO2	0.4	855	5.3	88 000	102.0
CO3	0.6	949	8.0	65 000	96.8
CO4	0.8	1 052	9.7	39 000	94.5
CO5	1.0	1 190	16.7	15 000	—
CO6	1.2	1 387	26.4	4 000	—

^aReaction carried out at 20°C in 80 ml of 1-octene solution in toluene, with 10 μmol of Zr, cocatalyst MAO, $[\text{Al}]/[\text{Zr}] = 1,000$, ethylene pressure 1 bar, polymerization time 60 min.

^bDetermined by ¹H-NMR analysis.

^cDetermined by viscosity measurements in decalin at 135°C.

^dMelting point of the copolymer.

Table 5

Ethylene/ α -olefins copolymerization with Cp_2ZrCl_2 in solution or supported on HY zeolite^a

Run	α -Olefin	Catalyst	Yield (g)	S.A. ^b	\bar{M}^c	α -Olefin in copolymer (mol %) ^d
CM1	4MP	Cp_2ZrCl_2	43.4	1 736	390	50.0
CM2	4MP	HY-MAO- Cp_2ZrCl_2	11.2	224	62 000	7.9
CM3	HEX	Cp_2ZrCl_2	46.9	1 876	1 240	50.0
CM4	HEX	HY-MAO- Cp_2ZrCl_2	17.4	348	19 000	22.1
CM5	OCT	Cp_2ZrCl_2	57.5	2 300	560	50.0
CM6	OCT	HY-MAO- Cp_2ZrCl_2	8.2	164	22 000	18.5

^aReaction carried out at 20°C in 80 ml of α -olefin (4MP = 4-methyl-1-pentene, HEX = 1-hexene, OCT = 1-octene), with 5 μmol of Zr in solution or 10 μmol of supported Zr, cocatalyst MAO, $[\text{Al}]/[\text{Zr}] = 2,000$, ethylene pressure 5 bars, polymerization time 60 min.

^bSpecific activity as $\text{kg}/\text{mol Zr} \cdot \text{bar} \cdot \text{h}$.

^cMean molecular weight determined by ¹H-NMR analysis for runs CM1, CM3 and CM5 and by viscosity measurements in decalin at 135°C for runs CM2, CM4 and CM6.

^dDetermined by ¹H-NMR analysis.

concentration of α -olefin (1-octene) (Table 4) according to what previously published concerning homogeneous catalysis [18]. This result is clearly correlated to the parallel increase of 1-octene incorporation as shown by the consequent T_m decrease. The chain transfer reaction to the comonomer and the presence of more labile tertiary hydrogens are responsible with reduced molecular weights while the increase of activity may be connected to the increased site accessibility with shorter and more swellable growing chains.

Following these results, the comparison in the catalytic behaviour for ethylene/ α -olefin copolymerization with Cp_2ZrCl_2 in solution and supported on zeolite was investigated by using α -olefins as reaction solvents (Table 5). The zirconocene in homogeneous phase brought to the exclusive formation of oligomers, in the range (estimated by NMR) 390–1 240 and characterized by terminal vinylidene bonds as evidenced through FT-IR and NMR analysis [26]. On the contrary, the zeolite supported catalyst gave, under the same experimental conditions, polymeric products with much higher molecular weights (up to two orders of magnitude), though with the usual depression in the catalytic activity. These elastomeric copolymers revealed a totally amorphous nature because of the high incorporation of α -olefin (in the molar range 8–22%), which was dependent on the type of

comonomer and anyway always below the value observed in solution. In this last case the oligomers are composed in all the cases by 50% moles of α -olefin but this evaluation is clearly of little significance in connection with the very low molecular weight. Again these experiments resulted in confirming a different discrimination by Cp_2ZrCl_2 towards the two olefinic monomers when supported on zeolite, in this peculiar case leading to totally different products compared to those obtained in solution.

4. Conclusion

A number of copolymerization experiments of ethylene with α -olefins were performed aimed at evaluating the effects of the supportation of HY zeolite on the catalytic behaviour of metallocene complexes. Preliminary treatment of the carrier with MAO, preventing ligand abstraction from the catalysts, brought to supported systems whose original nature was substantially maintained. A general decrease in the catalytic activity was observed probably because of the difficult access to the active sites, which at least in case of Cp_2ZrCl_2 seems to be confined in the inner pores of the zeolite. The copolymers obtained with supported catalysts showed higher molecular weights, indicating a minor incidence of the chain transfer reaction to

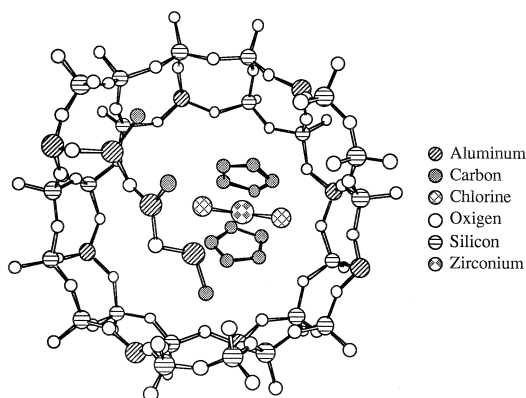


Fig. 1. Schematic representation of the interaction between Cp_2ZrCl_2 and the inner surface of MAO-modified zeolite.

the comonomer or β -hydride elimination, compared to what observed in solution.

Though a minor content of the α -olefin comonomer was incorporated in the products in the presence of supported Cp_2ZrCl_2 , no compositional difference was noticed in the case of stereorigid catalysts. The physical dimensions of the two types of complexes is probably responsible for their differentiated immobilization on the support. The biscyclopentadienyl complexes have indeed a molecular shape of the same dimension of zeolite supercage (7.2 Å diameter) and can be included in the inner cage of the crystalline support (Fig. 1). Clearly this is still to be considered as a work hypothesis needing further experimental evidence. In the proposed structure the functional groups on the modified zeolite internal surface are not indicated but their role appears to be of fundamental importance. This allows a major shape discriminating power towards the two monomers involved in the copolymerization process. This effect of the zeolite support was also confirmed by the increased selectivity with increasing the steric hindrance of the alkyl group around the double bond of the α -olefin.

In the case of α -olefins used as reaction solvents the employment of Cp_2ZrCl_2 in homogeneous phase exclusively brought to low molecular weight products. On the contrary the same complex on zeolite support was character-

ized by the formation of elastomeric polymers whose molecular weights resulted up to two orders of magnitude higher.

These results suggest that the Cp_2ZrCl_2 complex can be supported without substantial chemical modification in the inner pores of the zeolite where it keeps a catalytic behaviour as in solution whereas steric factors affect copolymers structure and molecular weight. The lower activity in the system investigated seems to be due to the increased molecular weight which reduces sites accessibility.

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References

- [1] H. Sinn, W. Kaminsky, H.J. Vollmer, R. Woldt, *Angew. Chem. Int. Ed. Engl.* 19 (1980) 390.
- [2] W. Kaminsky, M. Miri, H. Sinn, R. Woldt, *Makromol. Chem. Rapid Commun.* 4 (1983) 417.
- [3] T. Uozumi, K. Soga, *Makromol. Chem.* 193 (1992) 823.
- [4] J.C.W. Chien, D.H. He, *J. Polym. Sci. A: Polym. Chem.* 29 (1991) 1603.
- [5] M. Kaminaka, K. Soga, *Makromol. Chem. Rapid Commun.* 12 (1991) 367.
- [6] S. Collins, W.M. Kelly, D.A. Holden, *Macromolecules* 25 (1992) 1780.
- [7] M. Kaminaka, K. Soga, *Polymer* 33 (1992) 1105.
- [8] K. Soga, M. Kaminaka, *Makromol. Chem. Rapid Commun.* 13 (1992) 221.
- [9] W. Kaminsky, F. Renner, *Makromol. Chem. Rapid Commun.* 14 (1993) 239.
- [10] K. Soga, M. Kaminaka, *Makromol. Chem.* 194 (1993) 1745.
- [11] M.C. Sacchi, D. Zucchi, I. Tritto, P. Locatelli, T. Dall'Occo, *Macromol. Rapid Commun.* 16 (1995) 581.
- [12] D.W. Breck, *Zeolite Molecular Sieves*, 1st ed., Wiley, New York, 1974.
- [13] F. Ciardelli, A. Altomare, G. Arribas, G. Conti, F. Masi, F. Menconi, in: K. Soga, M. Terano (Eds.), *Catalyst Design for Tailor-Made Polyolefins*, Kodansha, Tokyo, 1994, p. 257.
- [14] G. Braca, G. Sbrana, A.M. Raspolli-Galletti, A. Altomare, G. Arribas, M. Michelotti, F. Ciardelli, *J. Mol. Catal. A: Chem.* 107 (1996) 113.
- [15] F. Ciardelli, A. Altomare, G. Conti, G. Arribas, B. Mendez,

- A. Ismayel, *Makromol. Chem. Macromol. Symp.* 80 (1994) 29.
- [16] S.I. Woo, Y.S. Ko, T.K. Han, *Macromol. Rapid Commun.* 16 (1995) 489.
- [17] K. Soga, M. Kaminaka, *Macromol. Chem. Phys.* 195 (1994) 1369.
- [18] R. Quijada, J. Dupont, M.S. Lacerda Miranda, R.B. Scipioni, G.B. Galland, *Macromol. Chem. Phys.* 196 (1995) 3991.
- [19] R. Quijada, G.B. Galland, R.S. Mauler, *Macromol. Chem. Phys.* 197 (1996) 3091.
- [20] E. Samuel, R. Setton, *J. Organomet. Chem.* 4 (1965) 156.
- [21] F.R.W.P. Wild, M. Wasiucionek, G. Huttner, H.H. Brintzinger, *J. Organomet. Chem.* 288 (1985) 63.
- [22] J.A. Ewen, L. Haspeslagh, J.L. Atwood, H. Zhang, *J. Am. Chem. Soc.* 109 (1987) 6544.
- [23] J.H. Elliott, *J. Appl. Sci.* 19 (1970) 2947.
- [24] J.C.W. Chien, B.P. Wang, *J. Polym. Sci. A: Polym Chem.* 28 (1990) 15.
- [25] W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, *Makromol. Chem.* 193 (1992) 1643.
- [26] M. Michelotti, A. Altomare, F. Ciardelli, P. Ferrarini, *Polymer* 37 (1996) 5011.