Characterization of Polyethylene Nascent Powders Synthesized with $TpTiCl_2(OR)$ Catalysts

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Summary: Different kinds of polyethylene and ethylene-1-hexene copolymers were synthesized with $TpTiCl_2(OR)$ (Tp = hydrotris(pyrazolyl)borate; R = Et, i-Pr, n-Bu) catalysts with and without H_2. The polymers were characterized by ^{13}C NMR, capillary viscosimetry or GPC, and DSC. The homopolymers showed properties characteristic of ultra-high molecular weight polyethylenes (UHMWPE) with linear structure and high density polyethylenes (HDPE) with molecular weights in the range of commercial grades under hydrogen atmosphere. The copolymers showed a 1-hexene incorporation up to 6 mol-%. Important differences in the thermal properties were observed between the first DSC (nascent powders) and the second DSC heatings (melt-crystallized samples), which evidenced the molecular weights influence on the melt-crystallized samples.

Keywords: hydrogen transfer; 1-hexene; nascent powders; polyethylene; $TpTiCl_2(OR)$

Introduction

Ethylene can be polymerized under various conditions to yield polyethylenes having markedly different chain structures and physical properties as a function of different structural parameters that influence their ultimate properties, such as type, amount and distribution of comonomer(s) and branching, average molecular weight (MW) and molecular weight distribution (MWD).[1] In the last few years, authors have pointed out that polyethylene reactor powders have a unique morphology and higher crystallinity than melt-crystallized or solution-crystallized samples.[2–4]

Better understanding of the nature of the nascent morphology of polyolefins, namely the formation and molecular organization of polymer particles initiated by heterogeneous or homogeneous catalyst systems in the reactor, and its related physical properties, is an important research topic.[2,5] The development of the nascent state morphology of polyolefins in the reactor is reasonably well understood on the micrometer level. However, at the molecular scale, the physical properties of nascent polyolefins are less clearly understood.[6,7] Although different catalyst types and synthesis conditions clearly play a role, there is no consensus on the origin of the high value for the peak melting point commonly seen in nascent polyethylene.[2,8–16] Interpretations which invoke chain-extended and/or fibrilar crystals,[8–11] strained noncrystalline tie points,[12,13] instrumental effects,[2] or small crystals which reorganize on heating,[14,15] have been invoked to describe aspects of the thermal behavior. Nascent samples of UHMWPE also exhibit a peak melting point which approaches the equilibrium value (T_m^0) for polyethylene, but is irreversibly lowered following a melt crystallization cycle.[2,10,14,16] In this sense, the nascent morphology of UHMWPE represents a unique combination of morphology, crystallinity and melting characteristics

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which is generally inaccessible via melt crystallization of polyethylene.[16]

Although the high melting temperature of nascent polyolefins is known for more than three decades, the thermal properties of polyethylenes made with non-metallocene precatalysts have not been investigated. The alkoxyl effect of $TpTiCl_2(OR)$ (R = Et, *i*-Pr, *n*-Bu) complexes on the polymerization of ethylene,[17,18] ethylene-1-hexene, and ethylene in the presence of H_2 have been recently investigated in our laboratories. The aim of the present work is the characterization the polymers obtained by these complexes in order to compare the physical properties of polyethylenes and the differences between nascent powders and melt-crystallized samples.

Experimental Part

The polymers were characterized by ^{13}C NMR using a JEOL 270 Spectrometer. The polymer samples were prepared in tetrachloroethane or 1,2,4-trichlorobenzene (TCB) in a 5 mm NMR tube. The 1-hexene content was calculated according to the ASTM X70-8605-2 method.[19]

Average molecular weights were measured in TCB with 0.2% v/v of IRGANOX® at 135 °C using a high temperature gel permeation chromatographer (GPC). The average molecular weights and the polydispersities were obtained using a universal calibration curve made with polystyrene standards. When the polymer was not dissolved in TCB, the viscosity-average molecular weights were established by one-point determination of the intrinsic viscosity measured from an Ubbehlode dilution viscometer in decalin stabilized with 0.2% v/v of IRGANOX® at 135 °C. The average viscosimetric molecular weights were determined using the Schulz-Blaschke correlation.[20]

The thermal properties of the polymers were analyzed in a METTLER TOLEDO, DSC822e calorimeter. The essays were carried out using the following procedure: polyethylene samples (3 to 10 mg) were sealed in an aluminium pan, heated at 10 °C/min from 25 °C to 170 °C (1st heating), kept 5 minutes at 170 °C isothermally, cooled at 10 °C/min from 170 °C to 25 °C, and finally heated at 10 °C/min from 25 °C to 170 °C (2nd heating). The analysis of the final curves led to the melting peak temperature (T_m) and the melting enthalpy (ΔH). The crystallinity degrees (X_c) were calculated using the expression ($\Delta H_{sample}/\Delta H_{theoric}) \times 100$, where ΔH_{sample} is the experimental value and $\Delta H_{theoric}$ is the melt enthalpy of crystalline polyethylene (290 J/g).[21] Additionally, the superheating phenomena was tested varying the sample mass, the first heating rate, and the temperature of isothermal treatment when the thermal history was erased.

Results and Discussions

The polyethylenes were characterized by ^{13}C NMR, capillary viscosimetry measurements and DSC. The ^{13}C NMR analysis of the polyethylenes showed a single signal of methylene group (CH_2) at 29.59 ppm. Signals corresponding to terminal methyl groups (CH_3) and tertiary carbon (CH) were not detected due to their relatively low concentrations with respect to the methylene groups (CH_2), which is an evidence that all polymers were mainly linear. Figure 1 shows the ^{13}C NMR spectra of the polyethylene made with $TpTiCl_2(OEt)$, which is representative of the all polyethylenes evaluated.

The capillary viscosimetry analysis showed that the average viscosimetric molecular weights (M_v) were strongly influenced by the alkoxyl ligands. As can be seen in Table 1, the M_v of the polymers increases as the $TpTiCl_2(OR)$ steric hindrance increases showing the following tendency: *i*-Pr > *n*-Bu > Et. This result suggests that the alkyl chain size reduces the ratio of chain transfer rate to propagation rate. This property allowed us to classify the samples as UHMWPE. The DSC analysis of the polyethylenes showed melting

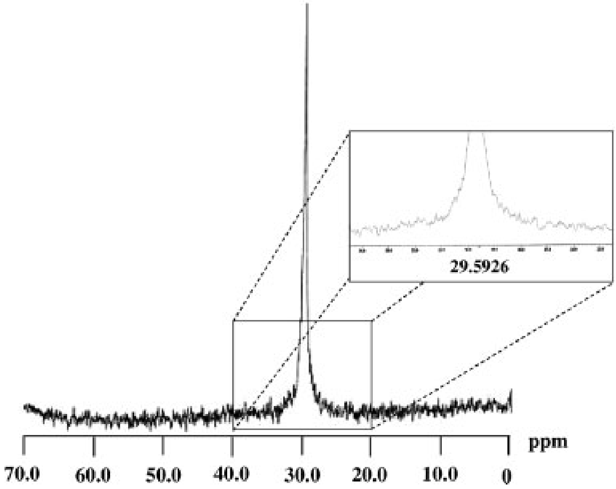

Figure 1.
^{13}C NMR of polyethylene produce by $TpTiCl_2(OEt)$.

temperatures around 138 °C and crystallinities between 39 to 47% (in the second heating), which agrees with UHMWPE characteristics.

The thermal properties between the nascent powders (1st heating) and the melt-crystallized samples (2nd heating) of these polyethylenes were significantly different. Although the melting temperature does not change significantly with the type of alkoxyl group used in the catalyst, there is a difference of almost 8 °C between the first and second heating. The nascent powder samples exhibit a high peak melting temperature at 145 °C, while the melt-crystallized samples show a lower peak melting temperature around 138 °C. This behavior might indicate that the crystals in the nascent polymer are better formed (larger) than the crystals formed after the first melt, which implies that the crystallization kinetics of nascent and molten polyethylene are different. However, superheating phenomena could possibly be present due to heat diffusion problems in the samples. Similar trends were found when comparing the crystallinities of the nascent polymers and melt-crystallized samples. In all cases, the crystallinities of the nascent powders were higher than those of the melt-crystallized samples, reaching values up to 76% and 47%, respectively.

Table 1.
Physical properties of polyethylenes.

Catalyst	$M_v \times 10^5$ (g/mol)	1st Heating		2nd Heating	
		T_m (°C)	X_c (%)	T_m (°C)	X_c (%)
$TpTiCl_2(OEt)$	23.3	145.8	69	137.7	39
$TpTiCl_2(OiPr)$	34.8	145.7	76	137.9	47
$TpTiCl_2(OnBu)$	25.6	145.2	75	138.0	46

Figure 2, 3 and 4 show the effect of sample mass (3, 5, 7 and 9 mg.), first heating rate (2, 5 and 10 °C/min), and the temperature of isothermal treatment when the thermal history was erased (170, 190, 210 and 227 °C) on the melting temperature and crystallitinity of the first and second heating for polyethylene made with $TpTiCl_2(OEt)$. As shown in Figure 2.a, the melting temperature of the first and second heating increases slightly (around 1 to 2 °C) with sample mass, remaining constant between 3 to 7 mg. This trend is in agreement with results reported the literature,[8–10] where superheating occurs when the sample mass increases. However, the differences in melting temperatures between the 1st and 2nd meltings when different polymer masses were used were the same in all cases

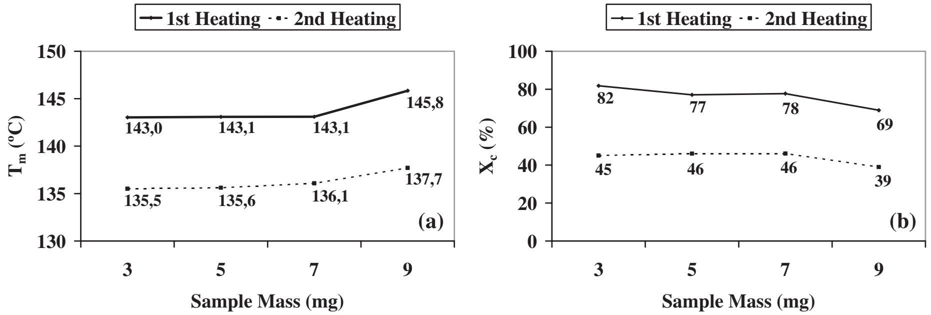

Figure 2.
Effect of sample mass on melting temperature (a) and crystallinity (b).

(around 8 °C). In contrast, the crystallinity presented an opposite behaviour to the melting temperature (Figure 2.b). It was observed that the crystallinity increases when the sample mass decreases. In agreement with other authors,[22] when the polymer is treated above the melting temperature, the entanglement density increases with the mass, reducing the chain mobility and hindering the crystallization. Despite of this fact, the differences of crystallinities between 1st and 2nd heatings for samples of different masses were the same in all cases (around 30%).

We also evaluated the influence of the 1st heating (thermal history erasing) at different rates (2, 5 and 10 °C/min) on these properties. As can be observed in Figure 3.a, the melting temperature increases around 4 °C between 5–10 °C/min (1st heating) with the heating rate. However, significant variations were not observed in the 2nd heating (2 °C approximately). In contrast, for both the 1st and 2nd heatings the crystallinity decreases when the heating rate increases (Figure 3.b), showing a maximum at 5 °C/min (45% and 79%, respectively). The differences in crystallinity were around 30% between each heating of each thermal history erasing rate tested. This behaviour is similar to the described in the sample mass case.

Some authors[23,24] have proposed that UHMWPE exhibits high concentration of tie molecules. When the nascent UHMWPE aggregates are heated up to 190 °C, the polymers retains its crystalline entities due to the long molecules entanglement points, which are present even after melting.[25,26] In this sense, the effect of the temperature of the isothermal treatment was analysed upon the melting temperature and crystallinity, as shown in Figure 4. Figure 4.a shows that, in the 1st heating, the melting temperature does not show a significant variation when the temperature of the

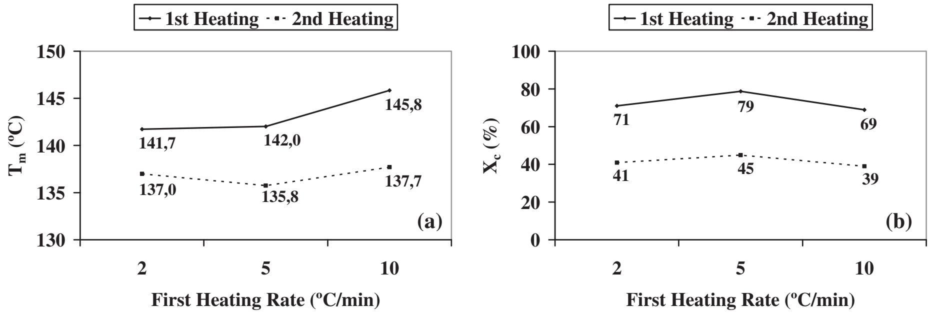

Figure 3.
Effect of first heating rate on melting temperature (a) and crystallinity (b).

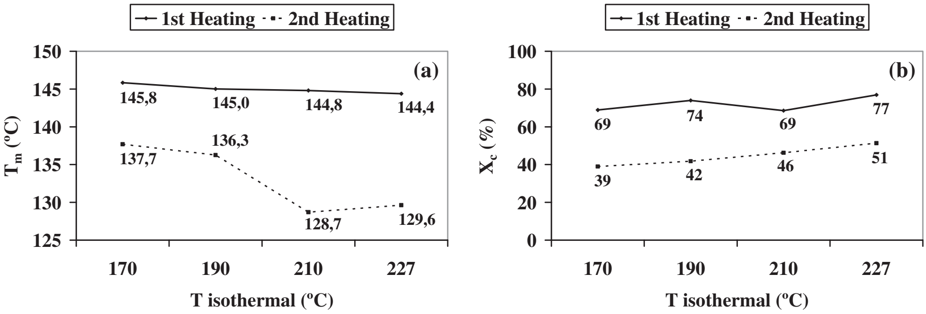

Figure 4.
Effect of isothermal temperature on melting temperature (a) and crystallinity (b).

isothermal treatment was increased. However, in the second heating, the melting temperature evidenced a significant drop (around 7 °C) when the nascent powder was heated over 190 °C. This behaviour might indicate that all crystalline entities initially present in the polyethylene were destroyed above 190 °C. Regarding the crystallinity, both 1st and 2nd heatings showed that the crystallinity increases with the temperature of isothermal treatment. In agreement with the literature,[23,26] this tend suggest that the tie molecules were completely destroyed during the melting process.

These experimental results indicated that the best DSC conditions for this kind of polyethylenes were: sample mass = 7 mg, heating rate = 10 °C/min and isothermal temperature treatment = 170 C, which were used to evaluate the polymers obtained by the other systems.

For the $TpTiCl_2(OR)/MAO$/ethylene/1-hexene system, the copolymers were characterized by ^{13}C NMR, GPC and DSC. The

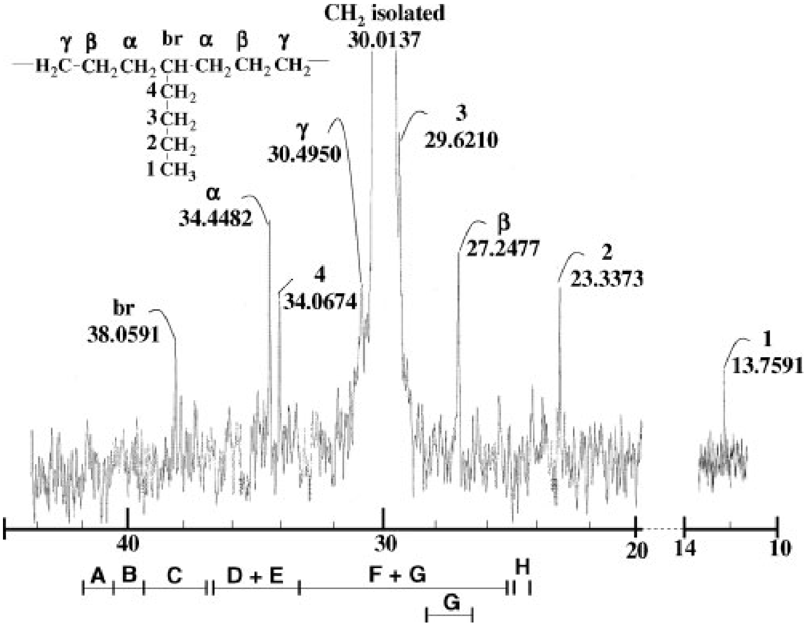

Figure 5.
NMR ^{13}C of copolymer made with $TpTiCl_2OEt$ complex ([1-Hex] = 0.5)

Table 2.
Physical properties of ethylene-1-hexene copolymers.

Catalyst	[1-Hex]	C_6	$M_w \times 10^5$ (g/mol)	M_w/M_n	1st Heating		2nd Heating	
	(M)	mol-(%)			T_m	X_c	T_m	X_c
					(°C)	(%)	(°C)	(%)
$TpTiCl_2(OEt)$	0.3	3.3	18.7	28	136.7	59	130.2	48
	0.4	2.2	14.8	27	137.2	59	130.7	47
	0.5	6.1	10.4	25	134.2	60	126.8	49
$TpTiCl_2(OiPr)$	0.5	1.2	6.2	21	135.7	58	128.8	47
$TpTiCl_2(OnBu)$	0.5	3.4	16.4	33	137.0	64	129.5	47

presence of 1-hexene in the copolymer was analyzed by ^{13}C NMR. Figure 5 shows an spectrum of a copolymer made with $TpTiCl_2(OEt)$ which is representative of those made with $TpTiCl_2(OR)$ complexes. According to the ASTM X70-8605-2 method, all the spectra showed characteristic signals of ethylene/1-hexene copolymers.

As seen in Table 2, the 1-hexene content in the copolymers synthesized with $TpTiCl_2(OEt)$ for the established comonomer concentrations showed a higher value at 0.5 M (6.1 mol %). The lower 1-hexene content (1.2 mol %) was obtained with $TpTiCl_2(O\textit{i}Pr)$, which was attributed to catalyst steric effects. The average molecular weights of the copolymers made with $TpTiCl_2(OEt)$ decreases from 18.7×10^5 to 10.4×10^5 g/mol as the 1-hexene concentration in the feed was increased (0.3–0.5 M). These results are in agreement with the propagation rate of comonomer insertion and 1-hexene concentration. The copolymers showed wide molecular weight distributions, as can be noted in Table 2, in agreement with the results obtained by Nakazawa et al.,[27] Jordan et al.,[28–30] and our previous study[18] on ethylene polymerization. This fact is an evidence that more of one active species is present in the catalyst.

On the other hand, Table 2 shows the 1-hexene concentration effect on the 2nd melting temperature. The melting temperature did not vary significantly when the 1-hexene concentration in the feed was between 0.3–0.4. However, at the maximum 1-hexene concentration in the feed (0.5), the melting temperature drops down. This behavior might indicate that when the 1-hexene content in the copolymer increases, the side chains hinder the growth of crystal lamellae, bringing about a drop of melting temperature. The copolymers showed melting temperatures ranging from 126 to 131 °C and crystallinities between 47 to 49 %. Additionally, the effect of alkoxyl group type on thermal properties was not significant. All these properties allowed to infer that the obtained copolymers showed high molecular weights (around 10×10^5 g/mol) with low comonomer incorporation (up to 6 mol-%).

A difference of 15% was observed when the thermal properties of the nascent powders (1st heating) and the melt-crystallized sample (2nd heating) of the copolymers were compared. A similar behavior was found in the homopolymers (Table 1), which showed a difference of 30% in its crystallinities. The lower difference observed in the copolymers case can be a consequence of the entanglement density reduction as a result of lower molecular weights present in the copolymers. This behavior allows higher chain mobility during the crystallization process.

For the $TpTiCl_2(OR)$/MAO/ethylene/H_2 system, the homopolymers were characterized by ^{13}C NMR, GPC and DSC. The results are summarized in Table 3.

The ^{13}C NMR analysis of the polyethylene samples showed a single signal of methylene group at 29.5 ppm, which shows that all polymers were linear. It is worthy mentioning that the weight average molecular weights (M_w) were strongly influenced

Table 3.
Physical properties of polyethylenes made in the presence of H_2.

Catalyst	$P_{ethyl/hydrogen}$ (-)	$M_w \times 10^5$ (g/mol)	M_w/M_n	1st Heating T_m (°C)	1st Heating X_c (%)	2nd Heating T_m (°C)	2nd Heating X_c (%)
$TpTiCl_2(OEt)$	10: 1	5.23	10.2	141.2	72	139.0	67
	7: 1	2.24	6.3	141.7	68	140.1	65
	5: 1	1.04	9.3	137.6	77	138.4	75
$TpTiCl_2(OiPr)$	5: 1	0.72	4.8	140.2	80	138.7	73
$TpTiCl_2(OnBu)$	5: 1	0.58	8.5	138.9	62	138.1	67

by hydrogen pressure (Table 3). Thus, when the $P_{ethylene/hydrogen}$ ratio was increased, the M_w increased from 1.04×10^5 to 5.23×10^5 g/mol. This tendency was expected in accordance with industrial practice, where the decrease of the hydrogen pressure reduces the probability of the transfer reaction to occur as a consequence of the drop of the hydrogen concentration in the reaction medium around the active site. On the other hand, the polyethylene polydispersities were lower than the copolymers case. This might indicate that, for the catalytic systems evaluated, hydrogen is capable of inhibiting a fraction of active species during the polymerization.

The polyethylenes showed melting temperatures in the interval from 138 to 140 °C and crystallinities between 65 to 75%. Additionally, no significant effects on thermal properties were observed when the type of alkoxyl group was changed. The characterization results evidenced that all the properties corresponded to a high density polyethylene (HDPE) with molecular weights in the range of commercials grades.

As seen in Table 3, it was found that the melting temperature and crystallinity did not show significant variation between the 1st and 2nd heatings. This behaviour shows that molecular weight has an important influence on the thermal properties of the melt-crystallized sample: the differences in the thermal properties between the nascent powders and the melt-crystallized samples were higher when the molecular weight increased.

Conclusions

The characterization by ^{13}C NMR, capillary viscosimetry or GPC, and DSC, showed that the catalytic system has an important influence on the final properties of nascent powders. Important differences were observed between the thermal properties obtained from the first DSC heating (nascent powders) and the second DSC heating (melt-crystallized samples). This behaviour was attributed to the crystallization process during the polymer synthesis which likely leads to less entangled morphologies (better formed crystals) than those obtained with the melt-crystallized sample, due to the fact that the crystallization kinetics of the nascent and molten polyethylene are different. Furthermore, an important influence of the molecular weight on the melting temperature and crystallinity of the melt-crystallized samples was corroborated.

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[1] H. Knuuttila, A. Lehtinen, A. Nummila-Pakarinen, *Adv. Polym. Sci.* **2004**, *169*, 13.
[2] S. Ottani, R. S. Porter, *J. Polym. Sci.: Polym. Phys. B* **1991**, *29*, 1179.
[3] Y. M. T. Engelen, P. J. Lemstra, *Polym. Comm.* **1991**, *32*, 3433.

[4] D. Hofmann, E. Schulz, D. Fanter, H. Fuhrmann, D. Bilda, *J. Appl. Polym. Sci.* **1991**, *42*, 863.

[5] J. Loos, M. Arndt-Rosenau, U. Weingarten, W. Kaminsky, P. J. Lemstra, *Polym. Bull.* **2002**, *48*, 191.

[6] S. Ottani, E. Ferracini, A. Ferrero, V. Malta, R. Porter, *Macromolecules* **1995**, *28*, 2411.

[7] R. A. Phillips, *J. Polym. Sci. Polym. Phys. B* **1998**, *36*, 495.

[8] H. D. Chanzy, R. H. Marchessault, *Polymer* **1967**, *8*, 567.

[9] H. D. Chanzy, J. F. Revol, R. H. Marchessault, H. Lamandé, *Kolloid Z. Z. Polym.* **1973**, *251*, 563.

[10] H. D. Chanzy, E. Bonjour, R. H. Marchessault, *Kolloid Z. Z. Polym.* **1974**, *252*, 8.

[11] E. Hellmuth, B. Wunderlich, *J. Appl. Phys.* **1965**, *36*, 3039.

[12] G. Delmas, *J. Polym. Sci. Polym. Phys. Edn.* **1993**, *31*, 2011.

[13] F. G. Morin, G. Sdelmas, D. F. R. Gilson, *Macromolecules*, **1995**, *28*, 3248.

[14] Y. M. T. Tervoort-Engelen, P. J. Lemstra, *Polym. Comm.* **1991**, *32*, 343.

[15] S. Rastogi, L. Kurelec, P. J. Lemstra, *Macromolecules* **1998**, *31*, 5022.

[16] R. A. Phillips, *J. J. Polym. Sci. Part B: Polym. Phys.* **1998**, *36*, 495.

[17] Karam, M. Jimeno, J. Lezama, E. Catarí, A. Figueroa, B. Rojas de Gascue, *Journal of Molecular Catalysis A: Chemical* **2001**, *176*, 65.

[18] Karam, E. Casas, E. Catarí, S. Pekerar, A. Albornoz, B. Méndez, *J. Mol. Catal. A: Chem.* **2005**, *238*, 233.

[19] M. De Pooter, P. B. Smith, K. K. Dohrer, K. F. Bennett, M. D. Meadows, C. G. Smith, H. P. Schouwenaars, R. A. Geerards, *Journal of Applied Polymer Science* **1991**, *42*, 399.

[20] *Polymer Handbook*, J. Brandrup, E. H. Immergut, Eds., 2nd edition, John Wiley & Sons, New York **1975**, p. V-14.

[21] J. G. Fatuo, *Morphology and Crystallization in Polyolefins*, Eds., C. Vasile, R. B. Seymour, *Handbook of Polyolefins*, **1993**, Marcel Dekker, Chapter 8.

[22] P. Smith, H. D. Chanzy, B. P. Rotzinger, *J. Mat. Scie.* **1987**, *22*, 523.

[23] L. Minkova, *Colloid Polym. Sci.* **1994**, *272*, 115.

[24] M. Mihailov, L. Minkova, E. Nedkov, R. Kircheva, *Makromol. Chem.* **1979**, *180*, 2351.

[25] M. Kresteva, E. Nedkov, A. Radilova, *Colloid Polym. Sci.* **1985**, *263*, 273.

[26] Z. Bashir, A. Keller, *Colloid Polym. Sci.* **1989**, *267*, 116.

[27] H. Nakazawa, S. Ikai, K. Imaoka, Y. Kai, T. Yano, *Journal of Molecular Catalysis A: Chemical* **1998**, *132*, 33.

[28] K. Minchue, R. F. Jordan, *Organometallics* **2004**, *23*, 460.

[29] K. Michiue, R. F. Jordan, *Macromolecules* **2003**, *36*, 9707.

[30] S. Murtuza, O. Casagrande, R. F. Jordan, *Organometallics* **2002**, *21*, 1882.