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Microstructural Characteristics and Thermal Properties of *ansa*-Zirconocene Catalyzed Copolymers of Propene with Higher α-Olefins

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Summary: Copolymers of propene and several higher α-olefins, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, and 4-methyl-1-pentene (4M1P), have been prepared with two different metallocene catalysts, *rac*-Et(Ind)$_2$ZrCl$_2$ (EI) and *rac*-Me$_2$Si(2-MeBenz-[*e*]Ind)$_2$ZrCl$_2$ (MBI), and comprehensively characterized by ^{13}C NMR spectroscopy. All copolymers produced with EI have comparable isotacticities as well as similar stereosequences. The copolymers produced with MBI significantly differ both from the reference propene homopolymer and among themselves: in fact, they are characterized by rather low isotacticities and the degree of tacticity is strongly influenced by comonomer type and concentration. A detailed ^{13}C NMR analysis revealed that these copolymers are constituted by highly isotactic and atactic sequences of various lengths. The similar thermal behavior, in terms of transition temperatures, for the homologues of the series obtained with the two different catalysts show that the capability of crystallization of these systems is not directly connected to the overall microstructural properties (e.g. the isotacticity index) but can be accounted for by the details of the microstructure.

Keywords: copolymerization; higher α-olefins; metallocene; microstructure; thermal behavior

Introduction

Recently it was revealed that a family of commercial random copolymers of propene with non conventional comonomers (e.g. odd comonomers such as 1-pentene) were characterized by an excellent combination of physical and mechanical properties compared to other commercial copolymers with commonly used comonomers, such as ethylene, 1-butene, or other even α-olefins.[1] The reason for the unique characteristics of these materials is still unknown. However these observations give clear evidence that copolymer properties depend on the

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content and distribution as well as on the type of the comonomer. Therefore we started a study aimed at investigating the effect of the kind of comonomer on microstructure and final properties of the copolymers. The research plan entailed two projects: i) study of propene/1-pentene copolymers with different comonomer content to investigate the effect of the comonomer amount; ii) study of the effect of length and branching of the comonomer through the investigation of copolymers of propene with different higher α-olefins.

The commercial copolymers are produced with traditional Ziegler-Natta catalysts. However, since multi-centered Ziegler-Natta catalysts do not allow meaningful correlations between microstructure and properties, for this investigation we used two single-site metallocene catalysts, which lead to well defined microstructures and uniform comonomer distribution:[2] the now classical and widely studied catalyst *rac*-$Et(Ind)_2ZrCl_2$, (EI), and *rac*-$Me_2Si(2\text{-}MeBenz\text{-}[e]Ind)_2ZrCl_2$ (MBI), which is one of the most successful isospecific catalysts. The choice was aimed at obtaining copolymers with different microstructures in order to examine the correlations between the ligand structure of the metallocene catalyst and the copolymer microstructural characteristics. A detailed ^{13}C NMR analysis of stereoregularity, and of comonomer content and distribution of all the samples was conducted. Furthermore, the investigation was addressed to the relationship between microstructural characteristics and thermal behavior of the copolymers.

Results and Discussion

Propene/1-Pentene Copolymers with Different Composition

Since 1-pentene is reported to yield superior properties to the resultant polymers, like outstanding clarity and gloss, the initial investigation focused on propene/1-pentene copolymers. Two series of propene/1-pentene copolymers with different compositions were prepared with EI and MBI. To assure that the comonomer concentration in solution remained nearly constant during the course of the reaction, the copolymerization conditions were selected to keep conversion of both comonomers lower than 5%. In Table 1 activities, feed and copolymer compositions together with some of their characteristics are reported. Moderately higher comonomer incorporation is in general observed with MBI than with EI, in line with the results from the literature.[2a] All copolymers possess narrow polydispersities, around 2. The reactivity ratio product indicates an almost random distribution of the

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Table 1. Homo- and copolymerization data for different propene/1-pentene copolymers

Run	**Catalyst**	**Feed ratio**[a)] **C_5/C_3**	**1-Pe (mol-%)**	**Activity**[b)]	**Mn*10^{-3} (g/mol)**	**Mw/Mn**	**$r_{P}r_{Pe}$**	**[mmmm]**[c)]
1	**EI**	Polypropene	-	28529	36	1.86	-	0.88
2		0.025	1.1	3881	67	1.72	n.d.	0.90
3		0.05	2.0	3639	67	1.71	n.d.	0.89
4		0.1	6.3	2706	42	3.21	1.51	0.88
5		0.2	10.6	4835	35	1.77	1.17	0.90
6		0.4	18.0	5094	34	1.71	1.16	0.91
7		1	36.4	2723	24	1.79	1.17	n.d.
8		1.5	40.7	2618	26	1.67	1.31	n.d.
9	**MBI**	Polypropene	-	42824	510	1.83	-	0.95
10		0.025	1.4	6734	440	1.99	n.d.	0.91
11		0.05	2.7	6926	370	1.95	n.d.	0.93
12		0.1	6.9	4223	240	2.01	1.11	0.86
13		0.2	10.3	3370	200	1.89	1.61	0.70
14		0.4	20.1	2538	170	1.76	1.12	0.53
15		1	38.6	2041	150	1.90	1.11	0.48
16		1.5	49.2	2782	140	2.32	1.07	0.37

Polymerization conditions: propene = 100 g; hydrocarbon solvent = 350 g; [Zr] = 2,5-10 · 10^{-6} mol/L; MAO/Zr = 6000 (molar ratio); T = 30°C; time = 30 min.

[a)] molar ratio pentene/propene in the feed;

[b)] activity expressed as: Kg polymer/mol catalyst produced in 1 hour;

[c)] molar fraction of isotactic pentads determined from the methyl (G) region (runs 1-14) and from the α-methylene (D) region (runs 15-16) of the ^{13}C NMR spectra.

comonomer ($r_{P}r_{Pe} \approx 1$) for both catalysts, independently of the ligand structure. These properties are in accordance with the single site nature of metallocene-based systems. A surprising result concerns the influence of the ligand structure on the copolymer stereoregularity. In fact, with the moderately isospecific catalyst EI, the isotacticity value of the propene homopolymer is maintained for the entire series of copolymers, while with the highly stereospecific catalyst MBI the isotacticity of the copolymers gradually decreases with increasing comonomer content.

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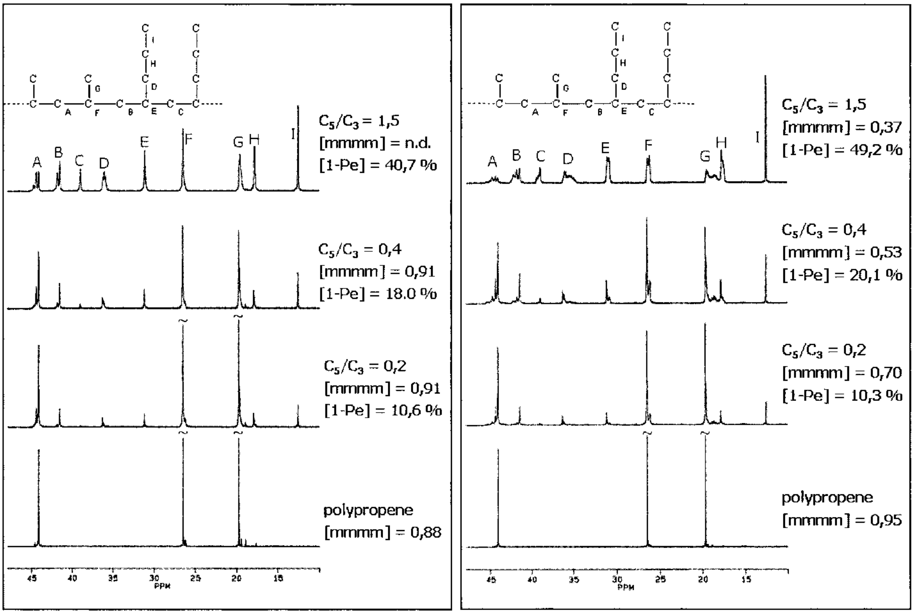

(a) (b)

Figure 1. ^{13}C NMR spectra of polypropene and propene/1-pentene copolymer samples prepared with EI (a) and MBI (b) at different compositions

Figure 1a shows the spectra of three copolymers prepared with EI at increasing comonomer content. The spectrum of the corresponding homopolymer is reported for reference purpose. It is apparent that the three copolymers are highly isotactic. Very narrow signals are observed in all spectral regions for the three copolymer compositions. Figure 1b shows the spectra of the corresponding copolymers prepared with MBI. One can easily appreciate the progressive loss of the stereoregularity with increasing incorporation of the comonomer. A progressive broadening of the signals occurs in all the spectral regions especially in those (G and D) more sensitive to steric effects. At the high 1-pentene content of 49% MBI behaves like an almost completely aspecific catalyst.

A more detailed analysis of the tacticity was conducted on selected samples. In the series of copolymers prepared with EI only the three pentads (mmmr, mmrr and mrrm), which correspond to the isolated steric errors, are detected (Table 2). On the contrary, in copolymers

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Table 2. Relative abundance of steric pentads for polypropene and some selected copolymers

Run	Cat	1-Pe (mol-%)	mmmm	mmmr	rmmr	mmrr	mrmm + rmrr	rmrm	rrrr	rrrm	mrrm
1	EI	0	0.881	0.053	-	0.045	-	-	-	-	0.021
4		6.3	0.879	0.057	-	0.037	-	-	-	-	0.027
5		10.6	0.900	0.044	-	0.036	-	-	-	-	0.020
6		18.0	0.910	0.036	-	0.036	-	-	-	-	0.018
9	MBI	0	0.950	0.023	-	0.020	-	-	-	-	0.007
12		6.9	0.865	0.031	0.010	0.022	0.023	0.013	0.008	0.016	0.012
13		10.3	0.695	0.052	0.031	0.044	0.053	0.040	0.023	0.031	0.031
14		20.1	0.528	0.040	0.052	0.082	0.105	0.081	0.044	0.033	0.035

produced with MBI (even when the comonomer content is as low as 6%) all possible stereosequences are present, including the rrrr syndiotactic pentad.

Copolymers of Propene with Higher α-Olefins

Two series of propene based copolymers with 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and 4-methyl-1-pentene (4M1P) were synthesized with the same catalysts EI and MBI, at a constant comonomer/propene feed ratio of 0.1 mol/mol. The selection of the comonomers allowed us to investigate the effect of gradually increasing comonomer length and of branching on the copolymer microstructure. In Table 3 activities, feed and comonomer amount together with some fundamental copolymer properties are reported. The data of the propene homopolymers are stated for reference purpose.

All copolymers feature narrow polydispersities and an almost random distribution of the comonomer ($r_P\ r_{Cm} \approx 1$) for both catalysts. However, here we will focus mainly on the differences between the two series. A first difference is given by the comonomer content. In fact, while similar comonomer incorporation is observed in most copolymers prepared with EI (with the only exception of the copolymer with the branched 4M1P having a comonomer content of only 2.6%), with MBI the comonomer incorporation ranges from 7.5% with 1-butene to 4.9% with 1-octene for the linear 1-olefins. Again, the lowest comonomer incorporation is observed with the sterically hindered 4M1P (3%).

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Table 3. Homo- and copolymerization data for propene/α-olefins copolymers

Run	**Cat**	**Cm**	**Incorp. Cm (mol-%)**	**Activity**[a)]	**Mn*10^{-3} (g/mol)**	**Mw/Mn**	**$r_{P}r_{Cm}$**	**[mmmm]**[b)]
1	**EI**	Polypropene	0	28529	36	1.86	-	0.88
2		Butene	6.8	2859	38	1.79	1.23	0.86
3		Pentene	6.3	2706	42	3.21	1.52	0.88
4		Hexene	6.1	4541	37	1.79	0.85	0.84
5		Heptene	5.7	6682	37	1.74	0.98	0.85
6		Octene	6.2	4147	23	1.65	1.23	0.88
7		4M1P	2.6	41	32	1.96	n.d.	0.88
8	**MBI**	Polypropene	0	42824	510	1.83	-	0.95
9		Butene	7.5	4615	150	2.81	1.48	0.83
10		Pentene	6.9	4223	240	2.01	1.11	0.86
11		Hexene	5.0	2054	230	1.93	0.99	0.72
12		Heptene	6.1	3838	200	1.89	1.06	0.79
13		Octene	4.9	1870	210	1.82	1.89	0.84
14		4M1P	3.1	369	110	2.03	n.d.	0.44

Polymerization conditions: propene = 100 g; Cm/C3 = 0.1 (molar ratio); hydrocarbon solvent = 350 g; [Zr] = 2,5-4.5 · 10^{-6} mol/L; MAO/Zr = 6000 (molar ratio); T = 30°C; time = 30 min.

[a)] activity expressed as: Kg polymer/mol catalyst produced in 1 hour;

[b)] molar fraction of isotactic pentads determined from the methyl (G) region of ^{13}C NMR spectra.

However, the most notable difference between the two series of copolymers concern the stereoregularity. All copolymers produced with EI feature isotacticities comparable with those of the reference propene homopolymer. The copolymers obtained with MBI differ significantly from the reference propene homopolymer as well as among each other. Indeed, the degree of tacticity is strongly influenced by the comonomer type.

In Figure 2 the NMR spectra of propene copolymers with 1-pentene, 1-heptene and 4M1P are compared. Among these three copolymers the isotacticity decreases with the increasing bulkiness of the comonomer. In the case of the propene/4M1P copolymer, the insertion of as little as 3% of 4M1P isolated units leads to a decrease of the isotacticity from 95 (homopolymer) to 44%.

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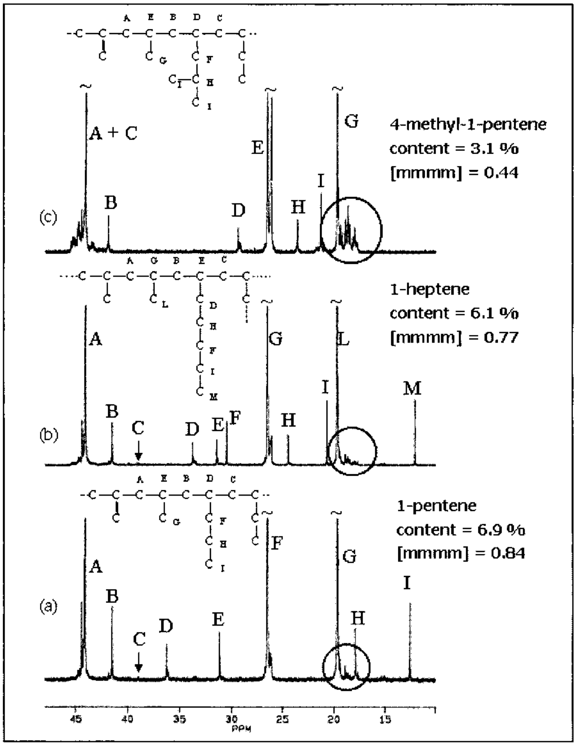

Figure 2. ^{13}C NMR spectra of propene copolymers with various comonomers prepared with MBI

Therefore, when MBI is used, the isotacticity of the copolymer strongly depends not only on the comonomer content but also on its length and structure.[3] These results are rather surprising since, to our knowledge, a similar effect has never been described for copolymers of propene with higher α-olefins obtained via metallocenes.[4] The quite obvious hypothesis that MBI contained impurities of the meso form of the metallocene and consequently the material was a mixture of isotactic and atactic chains formed on the racemic and meso isomer of MBI, respectively, does not seem to be likely for a certain number of reasons. First of all reproducible results were obtained with different catalyst batches, thus making the hypothesis of the presence of impurities of the meso form in the catalyst less probable.

Moreover, if the catalyst contained a mixture of the meso and racemic isomers, in principle

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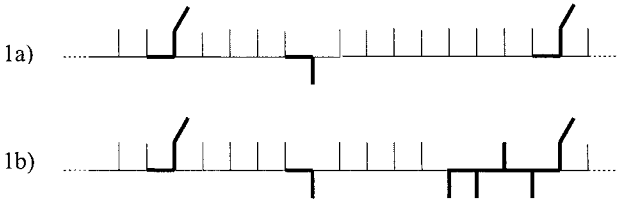
the ensuing copolymer should be a mixture of an isotactic and an atactic copolymer, the latter being likely characterized by higher comonomer content and lower molecular weight than the former. In fact it has been shown that, differently from propene, the higher α-olefins have remarkably greater polymerization activity with the meso form of dimethylsilyl bridged metallocenes than with the racemic one.[5] In this respect, fractionation performed with boiling *n*-pentane seems to indicate an uniform material although, due to the difficulty in performing an effective fractionation of this kind of copolymers, the results cannot be considered conclusive. Moreover, chain termination occurs more frequently on the meso than on the more sterically hindered racemic form.[5b] This is in contrast to the fact that all copolymers prepared with MBI, as well as those prepared with EI, are characterized by narrow molecular weight distribution and almost Bernoullian comonomer distribution, which are typical of single site catalysts.

We propose that the presence of a comonomer unit can occasionally lead to a loss of steric control of the more bulky MBI catalyst which lasts for several insertion events, thus leading to atactic blocks. At low comonomer content the atactic blocks are likely to be followed by isotactic blocks due to the recovery of the catalyst's steric control. When the comonomer incorporation reaches 30-40% there are only limited opportunities to regain the steric control prior to another comonomer insertion and the resulting copolymers are more or less atactic.

On the basis of this hypothesis catalyst EI should give a copolymer with the structure shown in Scheme 1a, i.e., a regular polypropene chain with defects due to isolated comonomeric units (for the sake of simplicity copolymers with low comonomer content are here considered) and only isolated (random) steric errors (besides other "normal" structural changes e.g. misinsertions), while with catalyst MBI (Scheme 1b) the copolymer chain would also contain more or less long atactic blocks, which might follow a comonomer unit.



Scheme 1

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Microstructure-Thermal Behavior Correlation

To ascertain the influence of the microstructure on the properties of these copolymers, an investigation on their thermal behavior was carried out by DSC analysis. After having destroyed the original crystallinity of the samples at a temperature well above the melting point of the propene homopolymers, the crystallization was performed under non-isothermal conditions (cooling rate –20°C/min) and the melting behavior was investigated during the second heating run.

Table 4 shows the melting temperatures of the two series of copolymers at increasing 1-pentene content. The thermal behavior of these copolymers is apparently contradictory since the two series prepared with the different catalysts, despite their noticeable differences in tacticity, show very similar trends of the melting temperatures. Indeed, rather similar T_m values are observed for almost all the pairs of homologues of the two series. If we compare, as a significant example, runs 6 and run 14 we notice that rather different isotacticities (0.91 and 0.53) correspond to very close melting points (60 and 63 °C).

Similar observations can be made by comparing the isotacticities and melting temperatures of

Table 4. Melting temperatures and microstructural parameters for the copolymers at increasing 1-pentene content

Run	Cat	1-Pe (mol-%)	[mmmm]	n_{iso}	T_m (°C)
1	**EI**	0	0.88	46.0	136
2		1.1	0.90	39.8	134
3		2.0	0.89	25.7	126
4		6.3	0.88	11.4	103
5		10.6	0.90	8.3	74
6		18.0	0.91	5.4	60
9	**MBI**	0	0.95	139.7	149
10		1.4	0.90	44.1	135
11		2.7	0.93	28.0	124
12		6.9	0.86	12.1	97
13		10.3	0.70	7.7	78
14		20.1	0.53	4.6	63

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Table 5. Melting temperatures and microstructural parameters for the copolymers with different α-olefins

Run	Cat	Cm	Incorp. Cm (mol %)	[mmmm]	n_{iso}	T_m (°C)
1	**EI**	Polypropene	0	0.88	46.0	136
2		Butene	6.8	0.86	11.2	118
3		Pentene	6.3	0.88	11.4	103
4		Hexene	6.1	0.84	11.6	94
5		Heptene	5.7	0.85	12.7	92
6		Octene	6.2	0.88	12.1	88
7		4M1P	2.6	0.88	19.7	119
8	**MBI**	Polypropene	0	0.95	139.7	149
9		Butene	7.5	0.83	10.9	125
10		Pentene	6.9	0.86	12.1	97
11		Hexene	5.0	0.72	13.6	91
12		Heptene	6.1	0.79	12.4	86
13		Octene	4.9	0.84	16.1	98
14		4M1P	3.1	0.44	12.3	106

the two series of copolymers of propene with different 1-olefins (Table 5). By comparing the two homologues with 1-hexene, runs 4 and 11, it is evident that despite the rather different isotacticities values (0.84 and 0.72), the melting temperatures are similar (94 and 91°C).

In order to correlate the thermal behavior with the microstructural features of these copolymers, we have calculated the average lengths of the isotactic sequences, n_{iso}, according to the following equation (deduced by microstructural data in a similar way as reported in the literature[6]):

$$n_{iso} = ([mmmm] + 4 \times [mrrm]) / ([mrrm] + [c_{Cm}])$$

where c_{Cm} indicates the concentration of the constitutional errors (isolated comonomer units, comonomer diads and triads) and, for both catalysts, only the concentration of the isolated steric errors [mrrm] is considered. The calculation is in fact based on the hypothesis that all the other steric defects observed with MBI are grouped into atactic blocks eventually following a comonomer insertion (see Scheme1b).

The rather similar thermal behavior for the homologues of the series prepared with the two different catalysts can be better understood if one correlates the observed transition

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temperatures to the n_{iso} values rather than to the overall isotacticity: the similar n_{iso} values in runs 6 and 14, 5.4 and 4.6 respectively, (Table 4), account for similar melting temperatures. The same considerations can be made for runs 4 and 11 of Table 5. The melting temperatures *versus* the calculated n_{iso} values for the two series of copolymers with 1-pentene are given in Figure 3; the plot suggests that the thickness of crystalline lamellae is correlated with the length of isotactic sequences.

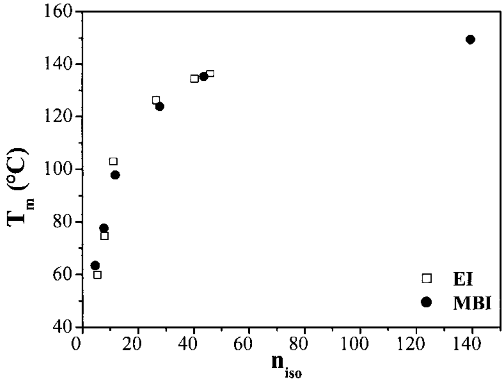

Figure 3. Melting temperatures *versus* the calculated n_{iso} values for the two series of copolymers at increasing 1-pentene content

The same trend holds for each pair of the series from the two different catalysts and suggests that the thermal behavior of the copolymers cannot be accounted for by the overall contents of isotactic pentads [mmmm], but it can be explained on the basis of the substantially equivalent average length of the isotactic sequences. At the same time the correlation observed between the thermal behavior and the n_{iso} values, calculated on the basis of copolymer structures as shown in Scheme 1, supports the reliability of the proposed structure for the copolymers from MBI as a succession of isotactic and atactic blocks, the latter likely formed by an occasional reversible loss of catalyst selectivity after a comonomer insertion.

Conclusions

In this paper several aspects relating microstructural characteristics and thermal properties of propene based copolymers to the kind and amount of the comonomer have been evidenced by introducing a series of comonomers with gradual increase of chain length and bulkiness. In

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particular, we observed that in the presence of higher α-olefins the catalyst MBI leads to copolymers whose microstructures seem to indicate that MBI shifts reversibly from a stereoselective to a non-stereoselective state. This leads to copolymers with new and interesting microstructures extremely useful for a fundamental study of the correlations between microstructural characteristics and final properties. In fact, by properly varying the type of comonomer and its concentration in the feed, it is possible to modulate the comonomer content and distribution as well as the length and frequency of the atactic blocks. Further studies are currently in progress to ascertain the nature of the interaction between the higher 1-olefins and the catalyst MBI and to understand the reasons why, under the chosen polymerization conditions, this phenomenon occurs.

Acknowledgements

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[2] see for instance: [2a] H.-H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem. Int. Ed. Engl.* 1995, *34*, 1143; [2b] S. Jüngling, R. Mülhaupt, U. Stehling, H.-H. Brintzinger, D. Fischer, F. Langhauser, *J. Polym. Sci, Part A: Polym. Chem.* 1995, *33*, 1305 and references therein.

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