Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Henschke, O. , Knorr, J. and Arnold, M.(1998) 'Poly-α-Olefins from Polypropene to Poly-1-eicosene Made with Metallocene Catalysts', Journal of Macromolecular Science, Part A, 35: 3, 473 — 481

To link to this Article: DOI: 10.1080/10601329808001990

URL: http://dx.doi.org/10.1080/10601329808001990

J.M.S.—PURE APPL. CHEM., A35(3), pp. 473–481 (1998)

POLY-α-OLEFINS FROM POLYPROPENE TO POLY-1-EICOSENE MADE WITH METALLOCENE CATALYSTS

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ABSTRACT

Linear α–olefins from propene to 1-eicosene have been polymerized using a zirconocene catalyst and a hafnocene catalyst. The resulting isotactic polymers were characterized by NMR, GPC and DSC analysis. Compared to the zirconocene products the molecular weights of the poly-α-olefins made with the hafnocene catalyst were higher. The molecular weight distribution was found to be narrow as expected for metallocene polymers. DSC measurements showed that side chain crystallization occurs for the polymers from poly-1-decene to poly-1-eicosene.

INTRODUCTION

In contrast to heterogeneous Ziegler-Natta catalysts homogeneous metallocene catalysts have only one kind of active sites. They are known as "single site catalysts" and produce polymers with a narrow molecular weight distribution.

Earlier investigations of poly- α-olefins synthesized with the heterogeneous catalyst system $TiCl_4/Al(iBu)_3$ showed that the melting points first decrease with increasing side chain length in the polyolefins, followed by an increase with further increase in length. The minimum is near poly(1-hexene) and poly(1-heptene) [1].

Highly isotactic poly-α-olefins from poly(1-decene) to poly(1-eicosene) were obtained with a Solvay type $TiCl_3/Cp_2Ti(CH_3)_2$ catalyst [2].

Our study describes the polymerization of propene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octa-decene and 1-eicosene and the properties of the poly-α-olefins with increasing side chain length. For the synthesis we used isospecific metallocene catalysts derived from the reaction of *rac*[(dimethylsilylene)bis(η^5-inden-1-ylidene)]zirconium dichloride and *rac*[(ethylene)bis(η^5-inden-1-ylidene)]hafnium dichloride with methylaluminoxane (MAO).

Because of regio-irregular insertions of propene units the melting point of metallocene polypropylene synthesized with $Me_2Si[Ind]_2ZrCl_2$/MAO or $Et[Ind]_2HfCl_2$/MAO is lower than the melting points of products made with heterogeneous catalysts [3, 4]. We investigated if differences in polymer structure and properties can be found for all poly-α–olefins in dependence on the used catalyst system.

EXPERIMENTAL

Materials

$Me_2Si[Ind]_2ZrCl_2$, $Et[Ind]_2HfCl_2$ and methylaluminoxane (10 wt% solution in toluene) were donated by Witco GmbH. The monomers were commercially obtained from Fluka. Propene and 1-butene were dried by passing through a molecular sieve 3A column. 1-Hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene were purified by distillation over calcium hydride. Toluene was refluxed over sodium/benzophenone.

Polymerization

Polymerization was carried out at 10°C with $Me_2Si[Ind]_2ZrCl_2$/MAO and at 30°C with $Et[Ind]_2HfCl_2$/MAO in a 0,5 dm^3 steel reactor. The reactor was filled with 250 mL toluene and monomer. Then, MAO in toluene was added and the reactor was thermostated. The polymerization was started by injection of the preactivated metallocene solution. The amount of metallocene catalyst used was $[Zr] = 6 \cdot 10^{-6}$ mol or $[Hf] = 6{,}25 \cdot 10^{-6}$ mol.

The molar ratio metallocene/methylaluminoxane was [Al]:[Zr] = 2000:1 or [Al]:[Hf] = 830:1. The monomer concentration was approximately 1 mol/L. The polymerization time was between 1 and 20 hours.

The polymerization was terminated by precipitation of the reaction mixture in diluted hydrochloric acid in methanol. The polymer was filtered, washed with methanol and dried in vacuum. The yields were in the range from 0.4 g to 7 g.

Characterization

Molecular weight and molecular weight distribution of the polymers were determined by gel-permeation chromatography (GPC) at 25°C in tetrahydrofuran or at 135°C in 1,2,4-trichlorobenzene.

The ^{13}C NMR spectra were recorded at 25°C on a Varian 500 spectrometer operating at 125 MHz. The solutions were made in $CDCl_3$.

The thermal behavior of the polymers was investigated using differential scanning calorimetry.

RESULTS AND DISCUSSION

In our investigations, the metallocene catalysts $Me_2Si[Ind]_2ZrCl_2/MAO$ and $Et[Ind]_2HfCl_2/MAO$ were used to polymerize α-olefins from propene to 1-eicosene in order to compare the influence of different catalysts on the polymer structure and properties. Both catalyst systems are known to produce isotactic polypropene. In this case the tacticity is lower for the hafnocene than for the zirconocene catalyst [4].

We obtained highly isotactic poly-α-olefins in the metallocene catalyzed polymerization of propene, 1-butene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene at 10°C with $Me_2Si[Ind]_2ZrCl_2/MAO$ and at 30°C with $Et[Ind]_2HfCl_2/$ MAO. The ^{13}C NMR spectra of poly(1-hexene) and poly(1-decene) which are shown as examples in Figure 1 illustrate that isotacticity is high for polymers made with both catalyst systems. Compared to the zirconocene the hafnocene catalyst is less stereospecific not only in propene polymerization but in the polymerization of higher α-olefins as well. This fact is indicated by differences in thermal behavior that will be discussed later but it is not visible in the poly(1-decene) spectrum in Figure 1.

Another difference between similar zirconocene and hafnocene catalysts that is known from propene polymerization is the fact that the hafnocene catalyst produces polymers with significantly higher molecular weights [4].

In order to reduce this difference we chose a lower polymerization temperature for the zirconocene catalyst. The polymerization results are summarized in Table 1.

The molecular weights of the poly-α-olefins synthesized with the zirconocene catalyst are about M_w = 50000 g/mol, that of the hafnocene products are higher.

There is a remarkable decrease in molecular weight from polypropene to poly(1-butene) (Figure 2) that is probably due to a stronger sterical hindrance of the

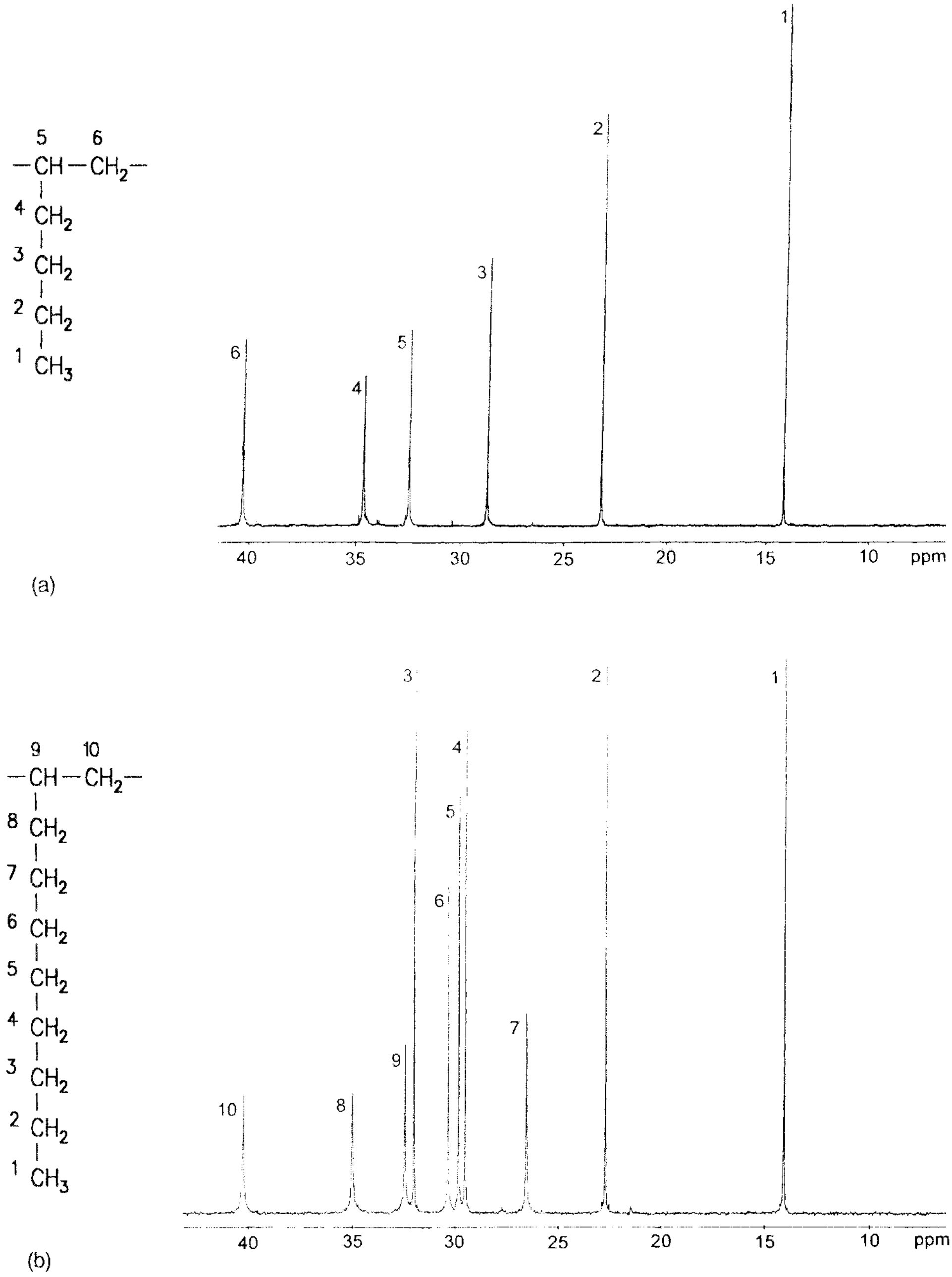
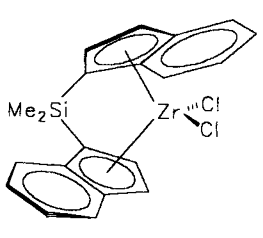
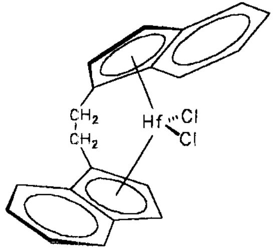


Figure 1. ^{13}C NMR spectra of poly(1-hexene) made with $Me_2Si[Ind]_2ZrCl_2$/MAO and poly(1-decene) made with $Et[Ind]_2HfCl_2$/MAO.

TABLE 1. Molecular Weight and Molecular Weight Distribution of Poly-α-olefins Synthesized with $Me_2Si[Ind]_2ZrCl_2$/MAO and $Et[Ind]_2HfCl_2$/MAO

Metallocene				
α-Olefin	M_w (kg/mol)	D	M_w (kg/mol)	D
propene	128	2,15	401	2,28
1-butene	29	2,26	107	2,01
1-pentene	34	1,56	84	1,78
1-hexene	37	1,52	95	1,75
1-octene	51	1,50	65	1,82
1-decene	45	1,78	67	1,6
1-dodecene	50	1,62	99	2,07
1-tetradecene	50	1,69	116	1,53
1-hexadecene	70	1,89	103	2,52
1-octadecene	68	1,85	70	1,94
1-eicosene	47	1,86	101	1,94

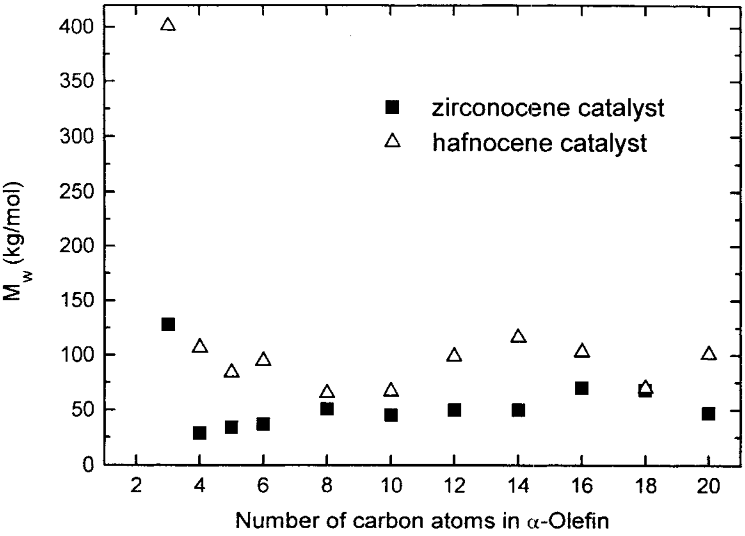


Figure 2. Molecular weights of poly-α-olefins synthesized with $Me_2Si[Ind]_2ZrCl_2$/MAO and $Et[Ind]_2HfCl_2$/MAO.

higher a-olefins at the active site of the metallocene catalysts during polymerization and a favoring of the termination reaction in comparison with propagation. The stronger hindrance may occur in α-olefin coordination and insertion steps because of their *n*-alkyl group compared to the methyl group of propene.

In both series the molecular weights of the poly-α-olefins do not differ much with increasing side chain length. But because of the increasing molecular weight of the α-olefin monomers the average degree of polymerization is significantly lowered from poly(1-butene) to poly-(1-eicosene).

The values of the ratio of weight- to number-average molecular weights for all poly-α–olefins made with the zirconocene and hafnocene catalysts are in the range from 1,5 to 2,5 (Table 1). This narrow molecular weight distribution is typical of metallocene catalyzed olefin polymerization [3]. In contrast to these values heterogeneous catalysts produce poly-α-olefins with a broad molecular weight distribution and $M_w/M_n = 4 - 32$ [1, 5].

The thermal properties of the poly-α-olefins synthesized with both metallocene catalysts were studied by means of differential scanning calorimetry (Table 2).

From polypropene to poly(1-octene) the glass transition temperatures decrease with growing length of the flexible side chain as expected from earlier investigations [6]. For the higher poly-α-olefins we could detect the glass transition temperature of poly(1-dodecene) at around -107°C.

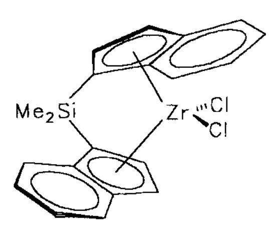
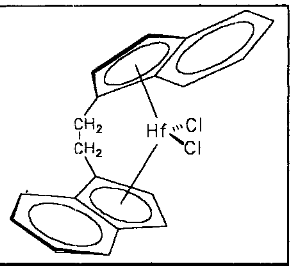
The melting points of the poly-α–olefins synthesized with both metallocene catalysts (Figure 3) follow the same trend that was found for polymers made with heterogeneous catalysts [1].

From polypropene to poly(1-pentene) the melting points decline, poly-(1-hexene) and poly(1-octene) were found to be amorphous and from poly(1-decene) to poly(1-eicosene) we observed the appearence of two separate melting peaks and increasing melting points.

For poly(1-butene) made with the hafnocene catalyst and poly-(1-pentene) made with the zirconocene catalyst two melting points occur because of different crystal modifications [7]. For the poly-α-olefins from poly(1-decene) to poly(1-eicosene) that show two separate endothermic peaks the second melting peak is caused by side chain crystallinity (Figure 4).

The melting peak at lower temperature is small. This low crystallinity level can only be assigned to main chain crystallinity. The other melting peak that is more distinct and shifted to higher temperatures with increasing length of the α-olefin can be assigned to side chain crystallinity. These assignments are in accordance with results from the literature [2, 8].

TABLE 2. Melting Points and Glass Transition Temperatures of Poly-α-olefins Synthesized with $Me_2Si[Ind]_2ZrCl_2$/MAO and $Et[Ind]_2HfCl_2$/MAO

Metallocene						
α-Olefin	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)
propene	-11,1	149,0	-	-8,1	137,9	-
1-butene	-15,6	110,7	-	-26,5	80,5	87,9
1-pentene	-33,2	68,0	74,0	-37,0	62,5	-
1-hexene	-45,2	-	-	-47,6	-	-
1-octene	-63,8	-	-	-63,9	-	-
1-decene	-	12,5	31,7	-	13,0	28,0
1-dodecene	-	39,9	46,5	-107	36,3	44,0
1-tetradecene	-	27,0	58,4	-	24,8	50,0
1-hexadecene	-	35,5	69,7	-	26,0	62,0
1-octadecene	-	43,1	74,9	-	37,0	68,0
1-eicosene	-	56,0	77,5	-	54,3	67,9

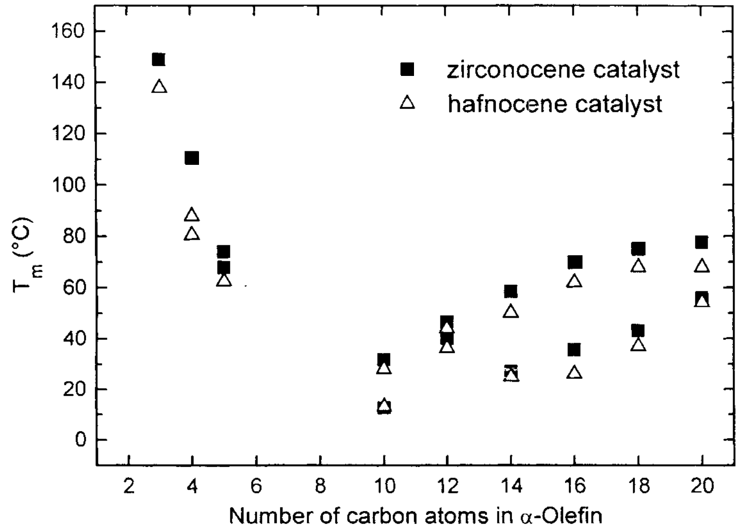


Figure 3. Melting points of poly-α-olefins synthesized with $Me_2Si[Ind]_2$-$ZrCl_2$/MAO and $Et[Ind]_2HfCl_2$/MAO.

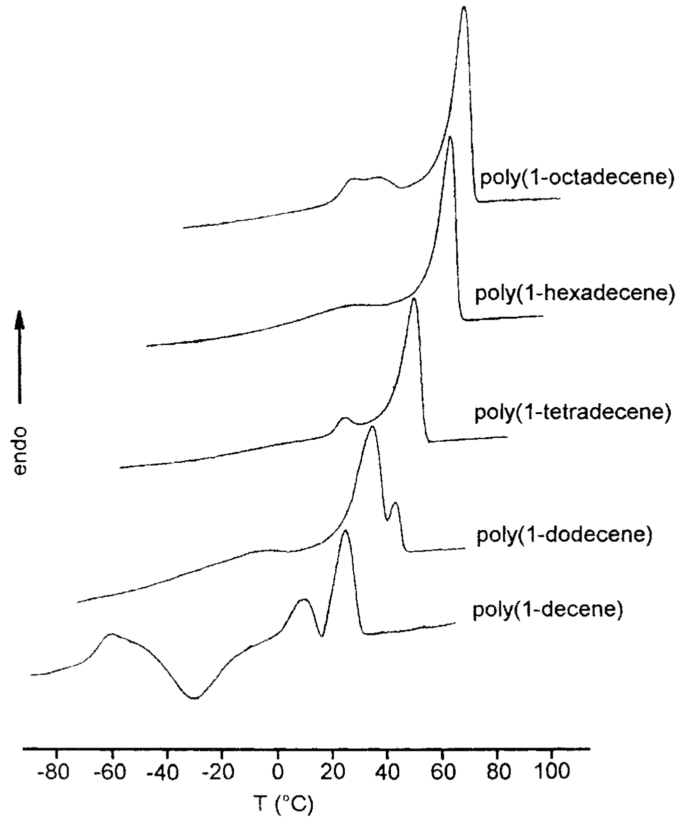


Figure 4. DSC heating curves for poly-α-olefins from poly(1-decene) to poly(1-octadecene) synthesized with $Et[Ind]_2HfCl_2/MAO$.

The melting points for the main chain as well as the melting points for the side chains are lower for the poly- α-olefins synthesized with the hafnocene catalyst in comparison with the zirconocene products (Figure 3). This result can be explained by a lower stereospecifity of the hafnocene catalyst and more stereoirregular insertions into the isotactic polymer chain. For the poly-α-olefins with longer side chains which are able to crystallize it is obvious that this irregular insertion affects not only main chain crystallinity but side chain crystallinity, too.

Compared to poly-α-olefins synthesized with heterogeneous catalysts [1] the melting points of all metallocene products are lower. The difference becomes smaller with increasing side chain length when side chain crystallinity is dominant. The melting points of poly(1-octadecene) that was synthesized with a heterogeneous catalyst or a zirconocene catalyst are equal [1].

CONCLUSION

It was shown that highly isotactic poly-α-olefins from polypropene to poly(1-eicosene) with narrow molecular weight distribution can be synthesized using a homogeneous zirconocene or hafnocene catalyst and that their properties differ from that of polymers made with heterogeneous catalysts but become more similar if side chain crystallinity occurs in poly-α-olefins with increasing side chain length.

ACKNOWLEDGEMENT

We are grateful to Dr. G. W. H. Höhne for carrying out most of the DSC measurements.

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Received July 8, 1997
Revision received October 20, 1997