

Properties of ethylene/1-octene, 1-tetradecene and 1-octadecene copolymers obtained with $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ catalyst: effect of composition and comonomer chain length

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Summary

Copolymers of ethylene and 1-octene, 1-tetradecene and 1-octadecene were synthesized in order to study the effect of the comonomer chain length and amount on density, melting temperature and heat of fusion. They were also compared with the properties of the copolymers obtained with the heterogeneous titanium catalyst.

It could be seen that the density/melting -area of the copolymers obtained with the zirconocene catalyst was much broader than with the titanium catalyst. It could also be seen that with the same comonomer content 1-tetradecene gave lower density of the copolymers than 1-octene. However, no difference were seen between the densities of the copolymers obtained with 1-tetradecene and 1-octadecene.

The melting temperature of the copolymers was seen to be the lower the longer the comonomer was. In the area of the high branching amount the linear correlation was not in work. It was also shown that the differences in the heat of fusions could only be seen at high amount of branches (> 15 branches/1000C): the longer the comonomer the lower amount of heat was needed to melt the copolymer.

Introduction

Metallocene catalysts can incorporate a broad range of comonomers, some of which in practice are unpolymerizable with the Ziegler-Natta systems. A good example is the use of bulky dienes (1) and the use of functional comonomers (2,3). The use of broad scale of different comonomers combined with the narrow comonomer and molecular weight distributions makes it possible to tailor the product for different end uses. With the metallocenes it is possible to obtain copolymers, where for example a comonomer having 18 carbon atoms could be polymerized efficiently (4,5). This would have not been possible earlier with the traditional heterogeneous catalysts.

The purpose of this study was to find out how the length of the α -olefins affect the density and the melting of the copolymer. Although these facts are well known in the industry and has been presented in numerous conferences and seminars (6,7) there seem to be a lack of information in the literature.

Experimental

Materials. Cp_2ZrCl_2 was commercial product (from Aldrich), methylaluminoxane was 10 weight-% in toluene, triethyl aluminium 10 weight-% in n-heptane (both from Witco) and n-heptane grade was GR (from J.T. Baker). The heterogeneous $\text{MgCl}_2/\text{TiCl}_4$ catalyst was made by ball milling and it was received from Neste Oy (present name Borealis Polymers Oy). Ethylene was grade 3.5 (from AGA) and 1-octene, 1-tetradecene, and 1-octadecene were for synthesis (from Aldrich). All the comonomers

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and n-heptane were further purified by conducting them through columns containing molecular sieves, CuO (BASF R3-11) and Al₂O₃, and ethylene before their addition to the reactor.

Copolymerization. Copolymerizations with the zirconocene catalyst were performed in n-heptane in a 1,0-dm³ stainless steel reactor. The molecular weight of the copolymers were controlled with the polymerization temperature (29 - 40 °C). The partial pressure of ethylene (2,2 - 2,6 bar) was set in order to keep the concentration of ethylene as 0,23 mol/dm³ in every run. The ethylene/1-butene copolymerizations with the titanium catalyst were performed in a 0,5-dm³ reactor with 300 cm³ amount of n-heptane. Ethylene partial pressure was 2,5 bar and 1-butene partial pressure was 0,6 bar at the highest. The polymerization temperature was 60 °C and Al/Ti mole ratio 200. The concentrations of ethylene and 1-butene were calculated according to Kissin (8).

Predetermined amount of n-heptane was added into the evacuated and N₂-flushed reactor. This was followed by liquid comonomer, which was pumped into the reactor. Total volume of the reaction medium was 700 millilitres in every run. Next, MAO/toluene solution was pumped into the reactor. Ethylene was added up to the polymerization pressure and it was controlled automatically with a pressure transducer and a magnetic valve. Copolymerization was initiated by pumping the catalyst/toluene solution into the reactor (in-situ start). The Al/Zr mole ratio was 1500.

Copolymerization was stopped by degassing the reactor, after which the organic layer was washed with a mixture of ethanol, diluted hydrochloric acid, and water. The polymer was precipitated with acetone after which it was filtered. The copolymers of ethylene and 1-tetradecene and 1-octadecene were further washed with acetone in order to extract the unreacted comonomer. The product was then dried under vacuum at 80 °C overnight.

Characterization. Comonomer content of the copolymers was determined with a Varian 400 Unity NMR spectrometer operating at 110 °C from the methylene, branching, α , β and γ carbons.

Molecular weight distributions were investigated with a Waters high-temperature GPC device equipped with three TOSOH mixed bed columns with exclusion limit for polystyrene 4×10^8 . Solvent 1,2,4-trichlorobenzene was used at a flow rate of 1.0 cm³/min. The columns were calibrated universally with broad molecular weight distribution linear low density polyethylenes.

Differential scanning calorimetry curves were obtained with heating rate 10 °C/min from -10 to 180 °C. The same sample was heated to the end temperature twice and between the runs it was cooled back to -10 °C with a cooling rate 10 °C/min. Only the second heating curve was analyzed.

Densities were determined in a water/ethanol gradient column at 23 °C. The values of the densities were recorded after 12 hours.

Results and discussion

The results of the copolymerizations made with the Cp₂ZrCl₂/MAO catalyst are seen in Table 1. It also shows properties of two commercial polyethylenes. It can be remarked that the synthesized copolymers all have the molecular weight at the same level and the only parameter was the comonomer and its amount.

In Table 2 the properties of the ethylene/1-butene copolymers obtained with the heterogeneous MgCl₂/TiCl₄/TEA catalyst system are presented.

The densities of the copolymers are plotted against the melting temperatures in Figure 1. There it can be seen that with the zirconocene catalyst it can be worked in much broader area than with the titanium catalyst in other words a wider density/melting area can be covered. A probable reason for this could be the narrower comonomer distribution in the metallocene copolymers than in the titanium

Table 1. Properties of the polymers used in the study.

Sample	Comonomer		Branches 1000C	\bar{M}_w g/mol	\bar{M}_w/\bar{M}_n	T_m °C	ΔH_m J/g	Density g/cm ³
	mole-%	weight-%						
HOMOI	-	-	-	65 000	2,6	136,6	157,4	0,965
OCT1	0,7	2,7	3,4	72 000	2,6	128,9	111,0	0,955
OCT3	1,9	7,1	9,4	81 000	3,1	120,9	82,4	0,934
OCT4	3,5	12,8	17,6	79 000	2,4	111,1	55,4	0,923
OCT8.2	5,3	18,3	26,5	72 000	2,1	100,7	37,1	0,902
OCT6	6,2	21,0	31,1	54 000	2,0	94,9	36,2	0,900
TET1	0,8	5,1	3,8	73 000	2,6	128,8	106,2	0,940
TET7.2	2,3	14,3	11,6	74 000	2,3	120,6	78,4	0,923
TET6	3,4	19,8	17,0	66 000	2,0	108,6	47,9	0,917
TET10.1	4,8	26,2	24,2	74 000	2,0	99,3	33,2	0,902
TET10.2	6,5	32,6	32,4	58 000	2,0	96,2	18,6	0,893
OD1	2,0	16,2	10,1	67 000	2,3	116,9	68,6	0,927
OD2	3,1	23,5	15,4	83 000	2,1	107,7	49,2	0,915
OD6.1	4,8	33,8	24,2	65 000	2,0	95,0	24,2	0,903
OD8.1	7,3	45,5	36,2	42 000	2,0	96,7	4,1	0,888
LLDPE*	1,6	6,0	7,9	111 000	3,6	126,3	98,2	0,922
HDPE*	-	-	n.d.	95 000	4,0	140,9	157,4	0,954

*) commercially available products

Table 2. Properties of the ethylene/1-butene copolymers obtained with Ziegler-Natta catalyst.

Sample	Comonomer		Branches 1000C	\bar{M}_w g/mol	\bar{M}_w/\bar{M}_n	T_m °C	ΔH_m J/g	Density g/cm ³
	mole-%	weight-%						
623	-	-	-	n.d.	n.d.	136,5	138,8	n.d.
624	0,6	1,2	2,9	n.d.	n.d.	130,4	119,4	0,930
627	1,3	2,6	6,7	720 000	6,4	126,4	104,7	0,926
625	1,8	3,5	8,8	600 000	7,4	125,3	105,3	0,923
626.2	2,6	5,1	13,0	545 000	7,3	123,5	93,7	0,921
626	3,9	7,5	18,9	500 000	11,8	122,4	86,1	0,914
626.1	6,1	11,5	29,6	379 000	11,1	121,2	58,5	0,908
627.1	7,4	13,8	37,1	246 000	9,1	120,6	39,4	0,893

copolymers. It can also be remarked that all the copolymer series contain comonomer up to 7 mole-%.

In Figure 2 the density of the copolymers is shown in dependence on the number of branches in the polymer chain. It can be seen that 1-tetradecene gave lower density of the copolymers than 1-octene. However, no difference were seen between the densities of the copolymers obtained with 1-tetradecene and 1-octadecene. It seems that the longer the comonomer is the more efficiently it reduces density. It also seems that with the same number of branches there is a upper limit for the length of the comonomer above which it do not reduce the density anymore.

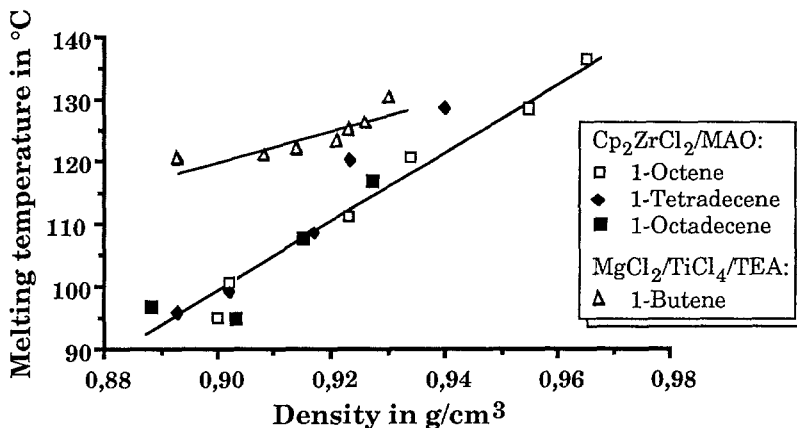


Figure 1. The correlation between density and melting temperature of the copolymers obtained.

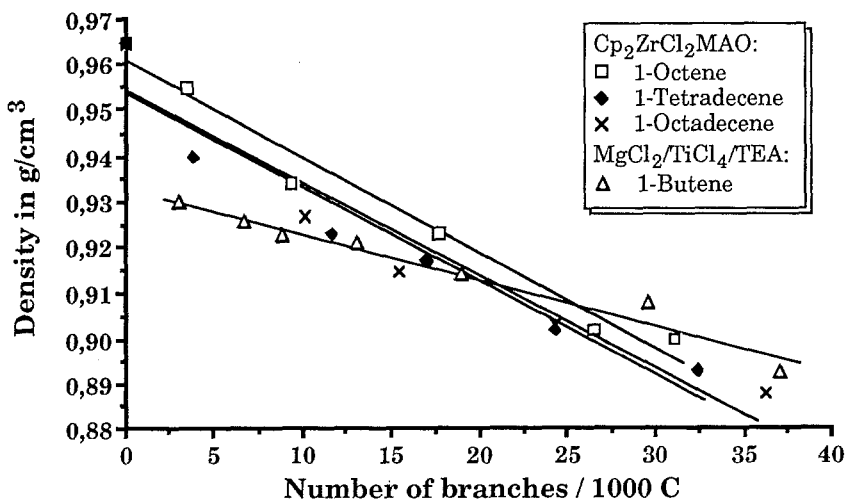


Figure 2. The correlation between the number of branches on the polymer backbone and the density of the copolymers.

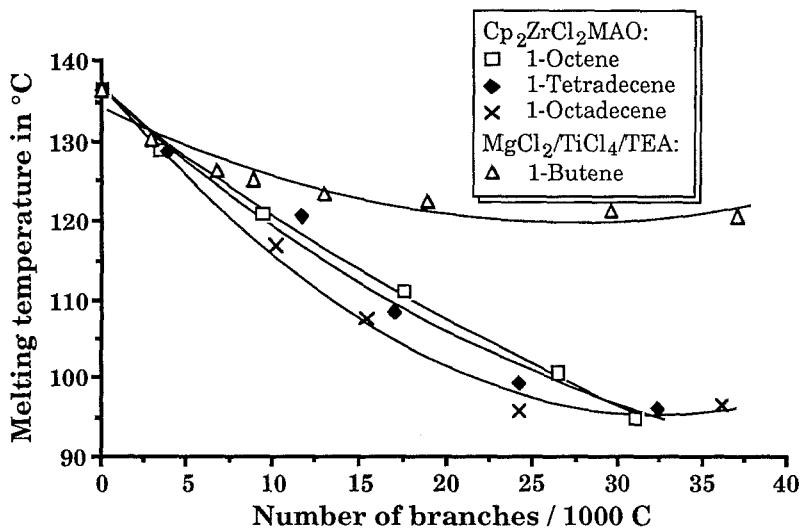


Figure 3. The correlation between the number of branches on the polymer backbone and the melting temperature of the copolymers.

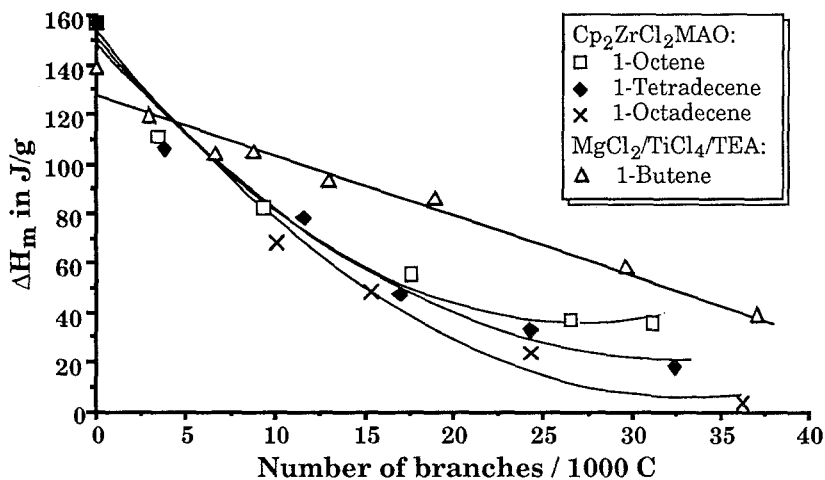


Figure 4. The correlation between the number of branches on the polymer backbone and the heat of fusion of the copolymers.

In the Figure 3 the melting temperature of the copolymers was seen to be the lower the longer the comonomer was. The same was seen earlier with the comonomers up to 1-octene (5). In the area of the high branching amount (>30 branches/1000C) the correlation did not work anymore. It can also be seen that the melting point of the copolymers obtained with Cp₂ZrCl₂/MAO catalyst decreases linearly to just under 100

°C, at which point it stops decreasing. The curve obtained from the copolymers made with Cp_2ZrCl_2/MAO catalyst resembles at high comonomer content the one obtained with $MgCl_2/TiCl_4/TEA$ catalyst. It seems that the copolymer is semicrystalline containing both homogeneous and heterogeneous features. It is also clear that the melting point can be varied over a much wider area with metallocene catalysts than with the heterogeneous titanium catalyst.

The heat of fusion in correlation with the number of branches in the copolymer chain is showed in Figure 4. There it can be noted that the differences are only seen at high amount of branches (> 15 branches/1000C): the longer the comonomer the smaller amount of heat is needed to melt the copolymer. Maybe the reason is that the longer comonomers disturb the formation of crystallites more efficiently than the shorter ones.

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