

Crystallinity and thermal properties of ethylene-1-decene copolymers

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Summary

Three copolymers of ethylene and 1-decene, covering a wide range of compositions, have been synthesized with a MgCl₂-supported Ziegler-Natta catalyst. The analysis by DSC and X-ray shows a great degree of heterogeneity in these copolymers and appreciable levels of crystallinity, corresponding to the orthorhombic lattice of polyethylene, are present even for very high 1-decene contents.

Introduction

Linear low-density polyethylene (LLDPE), obtained by copolymerization of ethylene and small contents of α -olefins, is receiving a considerable industrial and academic interest. Although the lower members of α -olefins are mostly used, higher terms are becoming attractive because of the improvement in some mechanical and rheological properties.

One of the most important characteristics of these LLDPE's is their heterogeneity in chemical composition, resulting from the existence of various kinds of active centres with different activity in the polymerizations with usual highly-active Ziegler-Natta catalysts. This heterogeneity, with a higher proportion of comonomer in the lower molecular weights (1,2), is reflected on a multimodal melting behaviour (1-4) and on a depression of the melting temperatures much smaller than that for other copolymers with similar comonomer content (5,6).

On the other hand, the increase on the length of the α -olefin lateral branch is reflected on a decrease of the reactivity of the comonomer in relation to ethylene, resulting in the difficulty of the obtention of copolymers with a high content on the α -olefin. Due to this aspect and to the fact that commercial LLDPE's incorporate only a small amount of α -olefin, very few articles cover a wide range of copolymer compositions.

The purpose of this work is to analyze the crystallinity and thermal properties of several ethylene-1-decene copolymers in a

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wide range of compositions, obtained with a heterogeneous Ziegler-Natta catalyst, trying to get more insight on the degree of homogeneity of these copolymers. The results are compared with those for other LLDPE's incorporating low members of α -olefins.

Experimental

Three copolymerizations of ethylene and 1-decene were carried out in a 1-litre glass reactor, with heptane as solvent, at a temperature of 70°C. A Ziegler-Natta catalyst of TiCl_4 supported on MgCl_2 and activated by Et_3Al was employed. The compositions of the copolymers were determined by ^{13}C -NMR in solution of 1,2,4-trichlorobenzene and the molecular weights were obtained by GPC in the same solvent, using the NBS 1475 polyethylene standard. The values of the composition and molecular weight for the different copolymers are presented in Table 1. The details of the synthesis and characterization of the copolymers have been reported elsewhere (7).

The thermal properties of these samples were measured by means of a Perkin Elmer DSC-7 calorimeter interfaced with a data station. The heating rate was 20°/min and the heat of fusion of a perfect crystal used in the determination of the crystallinity was taken as 290 J/g (8). The effect of the thermal history in the copolymers was analyzed by using two different crystallization conditions, starting from the melt: a rapid quenching (150°/min) and a slow cooling (2°/min).

The X-ray diffractograms were obtained in a Geiger Counter diffractometer from Philips Co., using nickel-filtered $\text{CuK}\alpha$ radiation.

Table 1.- Compositions, molecular weights and fractions of triad EEE (E = Ethylene) for the three ethylene-1-decene copolymers.

Copolymer	1-decene content ^a	$10^{-4} M_n$	[EEE]	
			Exp ^b	Calc ^c
CED1	55	1.50	0.271	0.091
CED2	11	1.01	0.735	0.705
CED3	6	1.72	0.824	0.830

a) In mol percent.

b) Ref. 7.

c) Calculated assuming a random copolymer.

Results and discussion

The DSC curves obtained for the three ethylene-1-decene copolymers are very similar in shape (although the enthalpy of melting is very different). Thus, figure 1 shows the thermograms of copolymers CED1 and CED3, quenched from the melt. As usual in LLDPE's, the melting curves extend almost from room temperature, reflecting the heterogeneous chemical composition characteristic of the copolymers synthesized with this kind of catalysts. However, the peak melting at higher temperature, arising from ethylene-rich chain segments, is much more dominant than in ethylene-1-butene copolymers (1,4), i.e. the bimodal behaviour is less apparent in these ethylene-1-decene copolymers.

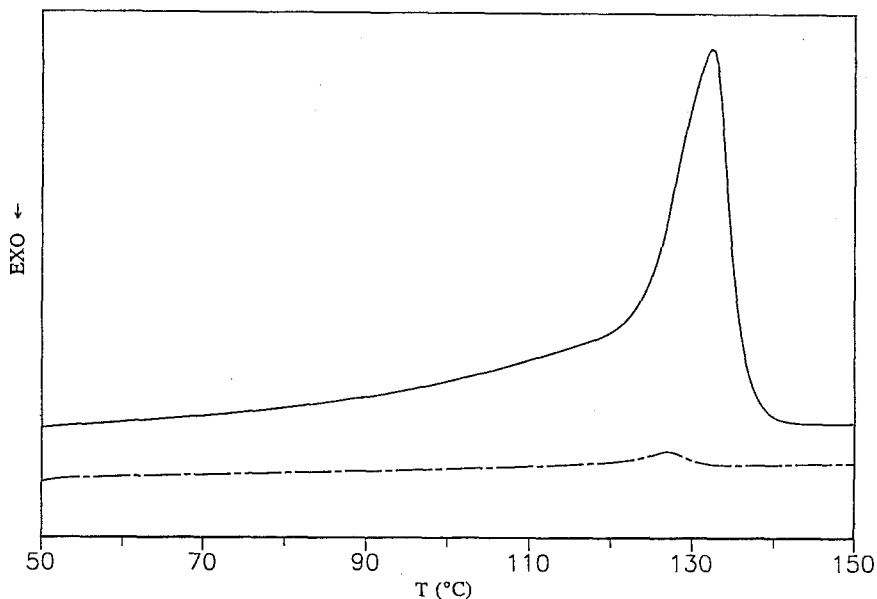


Fig. 1. DSC curves of CED1 (lower) and CED3 (upper) rapidly cooled from the melt.

The reason may be the increase on the differences in reactivity between ethylene and the comonomer on passing from 1-butene to 1-decene. These higher differences may have two effects. First, the chemical composition will be more heterogeneous, i. e., the differences in comonomer composition between high and low molecular weight chains are more important, leading to molecules with a much greater ethylene content than average. Second, important deviations from a random distribution of comonomer in our ethylene-1-decene copolymers have been found. These two effects are reflected, for instance, in the

discrepancies between the fraction of triad EEE calculated assuming random statistics and the experimental values (7), as it can be seen in Table 1. It is evident that the experimental values are substantially higher than the calculations for the copolymers with greater 1-decene content. The implication is the existence of ethylene-rich chain segments which are able to crystallize even in copolymer CED1, with very high 1-decene content (55 mole percent, 86 weight percent). For these high concentrations of 1-decene it can be entertain the possibility of the crystallization of 1-decene by itself. However, it has been shown that only the isotactic homopolymer is able to crystallize (9) and even in such case the crystallization is slow and the melting point is below or very close to room temperature.

The melting temperatures corresponding to the high temperature peak of the three copolymers are presented in Table 2. It can be observed that they increase as the comonomer content decreases. However, the differences in temperature are very small, having into account the great variation in 1-decene content. The explanation may be found again on the deviations from random behaviour, and on the heterogeneity of chemical composition.

Table 2.- Melting temperatures, enthalpies of fusion and crystallinities of the copolymers

Copolymer	T_m (K)	ΔH_m (J/g)	(1- λ)	
			DSC	RX
CED1	399	3	0.01	0.03
CED2	401	56	0.19	0.30
CED3	404	131	0.45	0.48

A measure of this heterogeneity can be obtained from the melting traces, which are usually bimodal for the most common LLDPE's: those with 1-butene as comonomer. Thus, a distribution index, DI, can be defined (1,4) as the ratio of the area of the lower temperature peak to the total enthalpy. Therefore, DI will be unity for a totally homogeneous copolymer, as the high temperature peak will be absent in such case. However, the low temperature peak of our copolymers is not so well differentiated and it appears more like a very long tail of the more prominent high melting peak. Nevertheless, a rough deconvolution of the melting curve leads to a value of about 0.5 for DI in the three

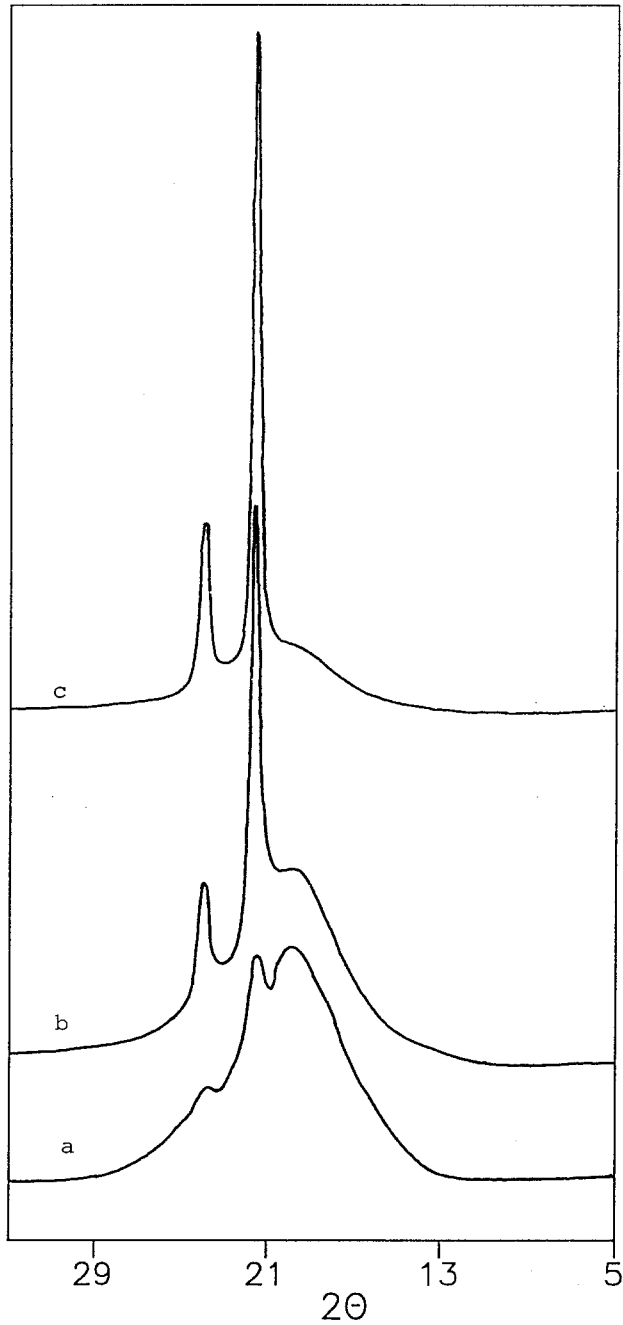


Fig. 2. X-ray diffractograms of the three copolymers cooled from the melt to room temperature. a) CED1, b) CED2 and c) CED3 (noise has been suppressed).

ethylene-1-decene copolymers. The higher heterogeneity of these copolymers becomes evident if we compare this value with that one of $DI \approx 0.8$ obtained for a copolymer of ethylene-1-butene synthesized with a similar catalyst system (4).

The crystallinity of these copolymers can be estimated from the total enthalpies of melting. The corresponding values are presented in Table 2. A very small but appreciable crystallinity is obtained for CED1. Higher levels of crystallinity are obtained if it is considered that only the ethylene segments are able to crystallize and the calculations are done in relation to the ethylene content in the copolymer instead of the total amount of sample (for instance, CED1 is only 14% by weight in ethylene). In any case, these crystallinities are much higher than those for homogeneous copolymers (5).

The samples were also analyzed by X-rays. The diffractograms corresponding to the three copolymers are shown in figure 2 (the thermal history imposed to the samples was a quenching to room temperature from the melt state). It can be observed that all the copolymers display the usual 110 and 200 reflections characteristic of the orthorhombic cell of polyethylene although the amorphous halo is increasing with the comonomer content. The crystallinities determined from these diffractograms are also presented in Table 2. These values are slightly higher than those from the enthalpy of melting, as it can be expected having into account that the interfacial content, usually of considerable importance in LLDPE's (6,10), is contributing in a different proportion to the two estimation methods: DSC and X-rays.

The effect of the thermal history on these copolymers was also analyzed. All the previous experiments have been performed on samples rapidly quenched from the melt. A second kind of thermal treatment was a slow crystallization (at $2^\circ/\text{min}$) from the melt. The DSC results show that the melting points are only slightly affected (they increase in no more than 2°C , when the samples are slowly crystallized). The same is true for the crystallinity, which shows an increase of less than 2%. This behaviour is parallel to that found for other LLDPE's (6,10).

In conclusion, the analysis by DSC and X-ray diffraction of three copolymers of ethylene-1-decene covering a wide range of compositions evidences a great degree of heterogeneity in these copolymers, as appreciable levels of crystallinity, corresponding to the orthorhombic lattice of polyethylene, are present even for very high 1-decene contents.

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