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Melting of functionalized polyethylenes with diethylmaleate

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Summary

The influence of the mole fractions and the chemical nature of the short branches on the level of crystallinity and on the melting temperature of functionalized polyethylene (PE) with diethylmaleate (DEM) was established. The results can be interpreted to yield two interesting points: the participant sequences in the crystallization decrease with the degree of grafting, which seems to indicate that the fanctionalization occurs at random, confirming evidences reported in the literature about the insertion on the secondary carbons. On the other hand, the study of the equilibrium melting temperatures, indicated that, the grafting increase the number of branches but not in a purely random arrangement. This last point clarify previous evidences obtained by FTIR, that report that grafting at the beginning of the reaction proceeds by radical attacks on the terminal unsaturations.

Keywords: Melting, polyethylene, functionalization, calorimetry, copolymers, crystallinity, grafting, crystallization, equilibrium melting temperature.

Introduction

Melting of copolymers depends on different features such as the nature or concentration of the chain units and their sequence distribution, among other variables. The equilibrium theory for the fusion of copolymers was proposed by Flory (1) obtaining a relationship between the depression of the melting temperature and the sequence probability of the crystalline counits. This sequence probability depends on the copolymer structure and, for a random copolymer, it can be identified with the mole fraction of the crystallizable units.

As predicted by theory, the melting temperatures depend on the counit content. They decrease monotonically with counit content and do not depend on the specific chemical nature of the counits. Very extensive analysis in polyethylenes have shown that ethyl, propyl, hexyl and vinyl acetate branches follow the same relation, other relatively small groups such as methyl and chlorine have higher melting temperatures (2). It has been pointed out that a proportion of these small groups may enter the lattice; meanwhile with side groups larger than methyl, the side groups do not enter the crystal lattice in systems crystallized from the bulk. Moreover, longer branches in polyethylene, originated from the method of synthesis or higher counits composition in the so called linear low density polyethylenes cause a broad and more diffuse melting (3).

In a general analysis on the fanctionalization of different polyethylenes in solution using diethylmaleate (DEM) as the functional monomer, one of the most important characteristics

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[t] In memoriam of a friend, a pioneer and an excellent educator, who throughout his life enriched the field of polymer science.

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is the thermal behavior of these systems. There are two points of interest in the melting of the functionalized polyethylene. One is related with the influence of the degree of functionalization on the melting temperature and the other on the relationship between the depression of these temperatures according to the Flory theory, and how the sequence arrangement of inserted DEM is identified in this type of analysis.

The purpose of the present communication is to reach some general conclusions about the molecular architecture of the functionalized chains and of the reaction mechanisms that originated them. Another aim of this work is to establish the relationship between the melting temperature and the crystallization conditions. In our knowledge and in spite of the vast literature about fanctionalized polyolefins, we have not found studies that deal with the melting and crystallization conditions close to the thermodynamic equilibrium. It is also the first time that a large number of well characterized PE samples with a wide range of fanctionalization degrees are considered.

Experimental

Materials

The original samples used in this study were commercial polymers. The high density (HDPE) and linear low density polyethylenes (LLDPE) were obtained from different manufacturers. It is important to point out that although the nomenclature HDPE is usually reserved for linear PE, the commercial samples used in this work are not totally linear because they are copolimerized with very low concentrations of α-olefins, lower than 1% molar. But due to their application fields they are marketed like HDPE, and for this reason this nomenclature was used in this work.

The samples were characterized previously to the modification, following conventional procedures. Molecular weight characteristics of the original PE are given in Table 1. Weight and number-average molecular weights were determined by gel permeation chromatography, GPC. The determination of the counit content in the PE was carried out by ^{13}C-NMR using the corresponding assignments given by Randall and Pooter (4,5). The type and concentration of α-olefin are summarized in Table 2. Densities of the samples were determined at 23 °C in a Davenport density gradient column, consisting of a water-ethyl alcohol mixture, calibrated with standard glass floats (Table 2). The densities were converted to degrees of crystallinity, $(1-\lambda)_d$ by the specific volume relationship given by Chiang and Flory (6).

Synthesis and characterization

Functionalization reactions were carried out with diethylmaleate (DEM) in solution of ortho-dichloro benzene (o-DCB) and the initiator was 2-5-dimethyl-2,5(di-t-butyl)peroxihexane(DBPH).

Table 1. Weight (M_w) and number-average molecular weights (M_n) of the polyethylene samples used.

Sample	M_w(g/mol)	M_n (g/mol)	M_w/M_n
HDPE-1	175.000	18.700	9 4
HDPE-2	313.000	17.700	17,7
HDPE-3	222.000	18.000	12,3
HDPE-4	144.000	23.000	6,2
HDPE-5	182.000	36.700	5,0
LLDPE-1	84.000	---	---
LLDPE-2	150.000	35.000	4,3
LLDPE-3	115.000	30.000	3,8
LLDPE-4	53.000	14.000	3,8

Reactions were carried out in a three-necked glass vessel equipped with a magnetic stirrer and using nitrogen atmosphere in order to avoid polymer degradation, following previously reported steps (7).

For the characterization of functionalized samples, infrared analysis and ^{13}C-NMR techniques were used. FTIR spectra were obtained using a Perkin Elmer 16 PC spectrometer after 20 scans at a resolution of 2 cm^{-1}. The grafted DEM in the samples was determined by using calibration curves for the systems reported elsewhere (7). Moreover, the analysis of the spectra obtained for both techniques demonstrated that the functionalization occurs by isolated units of DEM without detecting oligomers of DEM, either linked to the chain or homopolymerized.

Thermal characterization

Melting temperatures were determined in a Perkin Elmer, DSC-7, calorimeter, calibrated with indium. Between 10 to 12 mg of HDPE sample sealed in an aluminium pan were subjected to the following steps: heating at 10 °C/min from room temperature to 160 °C and, after 5 minutes at 160 °C, cooling at 10 °C/min from this temperature to 25 °C and, finally, heating at 10 °C/min from 25 °C to 160 °C to obtain the melting peak temperature (Tm). For the LLDPE samples the same procedure was applied, with the difference that the maximum temperature used was 145 °C.

In another set of experiments, the isothermal crystallization at different temperatures was studied in the calorimeter. The general procedures have been described previously (8). After isothermal crystallization, without previous cooling, the melting process was recorded at a heating rate of 5 °C/min.

Enthalpies of melting (and of crystallization) were converted to levels of crystallinity,$(1-\lambda)_{\Delta Hu}$ from the ratio $\Delta Ha / \Delta Hu$, being ΔHa y ΔHu the apparent and the completely crystalline heats of fusion, respectively. Taking for the enthalpy of a polyethylene crystal, ΔHu, the value of 69 cal/g (3).

Table 2. Structural Parameters determined by C^{13} NMR, densities and crystallinity of the polyethylene samples used.

Sample	Type of α-olefin	% Branch content (mol %)	Density (g/cm^3)	$(1-\lambda)_d$
HDPE-1	Cohexene	0,80	0,9465	0,677
HDPE-2	Cobutene	0,66	0,9493	0,695
HDPE-3	Cohexene	1,07	0,9433	0,657
HDPE-4	Cobutene	0,35	0,9530	0,719
HDPE-5	Cobutene	0,52	0,9420	0,648
LLDPE-1	Cohexene	3,40	0,9131	0,454
LLDPE-2	Cobutene	3,80	0,9210	0,508
LLDPE-3	Cooctene	3,90	0,9120	0,447
LLDPE-4	Cooctene	3,20	0,9200	0,502

$(1-\lambda)_d$ = degree of crystallinity obtained by density

Results and discussion

Degree of crystallinity

Figure 1 shows the results for the unmodified and functionalized samples obtained from the enthalpy of crystallization against the total molar % of branches.When the enthalpy of melting is used, the same values, are found. It is important to point out that the experimental points correspond to polyethylene samples in which the co-units are different, including the DEM. The most important result is that the degree of crystallinity decreases very rapidly with increasing the amount of branches, from 65% at 0.5 molar %, to about 32% at 5.7 molar %. It can be concluded that the reduction in crystallinity decreases with the concentration of branches and is independent of the chemical nature of the side groups. These results, which include a very wide range of branch contents, are in good agreement with those obtained from the analysis of ethylene-α-olefin copolymers (9-11). In those the rapid decrease of the crystallinity level with the short branch content is a consequence of the structure of the random copolymers. With increasing branch content, the number and size of the sequences which participate in the crystallization process is reduced (2). These facts seems to indicate that we are dealing, in principle, with random type copolymers, or more clearly with sequence distributions of branches (including the DEM) close to random.

It is important to point out that in isothermal conditions the crystallinity degree obtained is much lower than that obtained under dynamic conditions (see Fig. 1), which indicates that a percentage of crystallizable species does not enter in the process of isothermal crystallization.

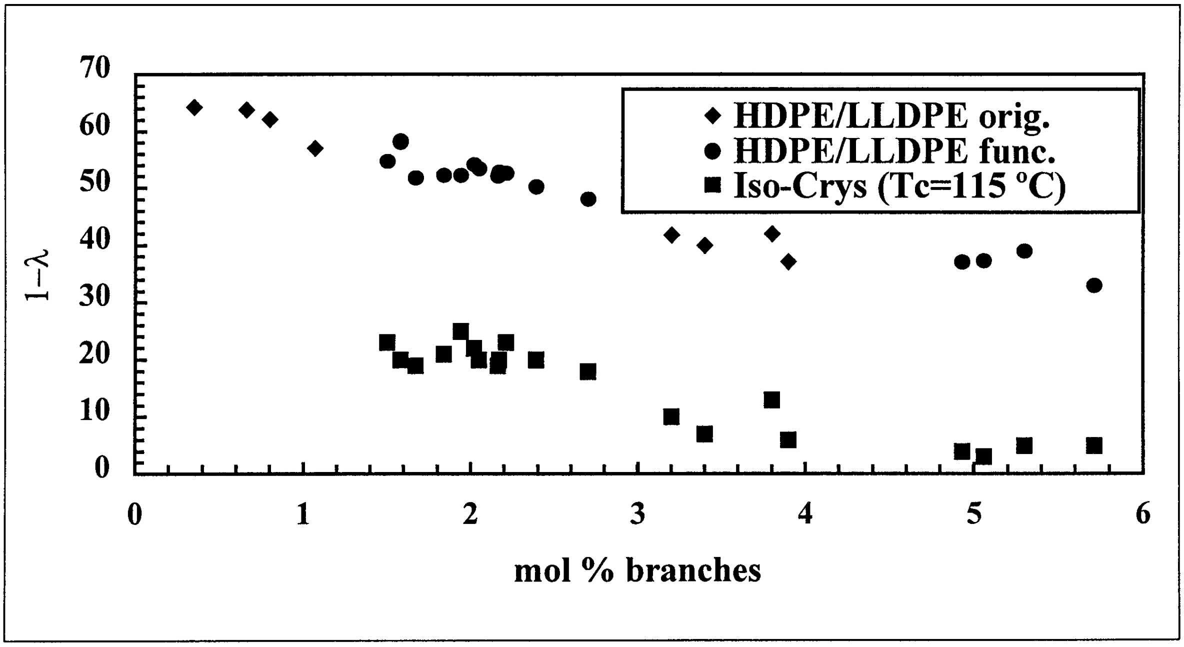

Figure 1. Crystallinity degrees obtained from the enthalpy of crystallization versus the total molar % of branches (α-olefin plus DEM): (a) In dynamic conditions for (◆) HDPE and LLDPE originals and for (●) HDPE and LLDPE functionalized (b) In isothermal conditions (at Tc=115 °C) for some (■) HDPE and LLDPE originals and functionalized.

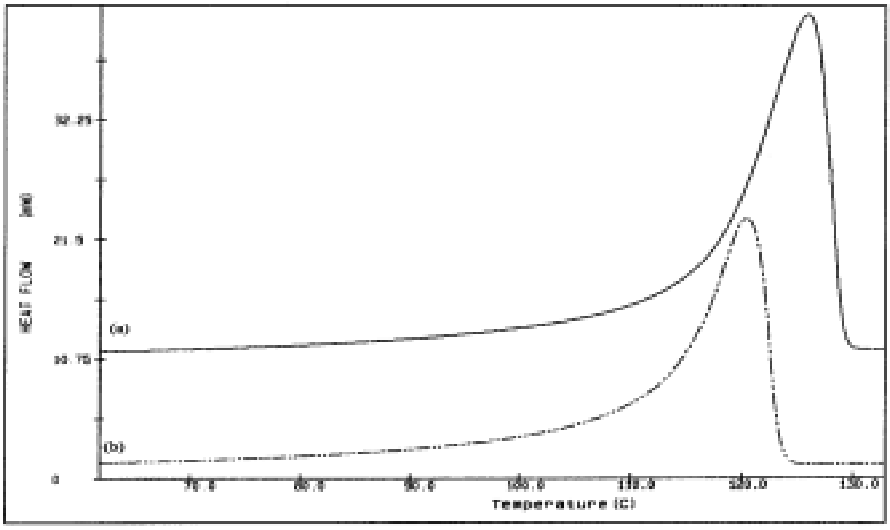

Figure 2. Comparison of DSC endotherms for (a) HDPE-2 original and (b) HDPE-2 functionalized (HD2FUN-39) with 1,55 mol% DEM.

Melting Temperatures

We limit this work to the analysis of the melting temperatures of a very wide range of ethylene-α-olefins copolymers with different side groups, including the functionalized samples (see Figure 2). In our samples, we do not have to consider variations on molecular weight and molecular weight distribution of the samples because they are in the same approximate range, the one in which there is not an important influence of molecular weight on the T_m values.

Table 3 shows the melting peak temperatures (T_m) obtained in dynamic conditions of all these samples. Again, in a similar way to the degree of crystallinity, the melting temperatures of the samples display the same relation with the branch content. In such way that the T_m's are independent of the chemical nature of the side group, but an important depression with respect to the equilibrium melting temperature of polyethylene ($T_m° = 145.5$ °C) can be appreciated in the values. The apparent melting temperature is about 130 °C for the sample with the lowest branch content (0.35 mol %) and decreases down to 116 °C, for the samples with the highest branch content (5.7 mol %). Although, it is important to point out that the T_m's obtained after isothermal crystallization are higher than those obtained under dynamic crystallization procedure (see Fig. 3). The differences correspond to the melting of larger crystallites obtained at lower undercoolings.

On the other hand, it is important to notice that the obtained DSC endotherms show the homogeneous pattern of the functionalized samples in spite of the depression that was reflected in the T_m and in the heat of fusion. Figure 2 shows the endotherms for the sample HDPE-2, and for a functionalized sample obtained from it, where the functionalized polymer do not show any traces of heterogeneous structures, as judged from the shape of the endotherm, not even any small shoulder. Although, in the case of the LLDPE their DSC endotherms showed a small shoulder, that was more pronounced in the functionalized sample obtained from them, in any case the grafting did not originate a very broad and more diffuse melting, characteristic of a PE with chain irregularities (long branches for example)(3).

Moreover, the qualitative comparison seems to indicate that there are differences in the microstructure when the functionalization takes place in the HDPE samples or in the LLDPE samples.

Equilibrium melting temperatures (T_m^0)

Previous analysis of grafted samples obtained by IR spectroscopy have suggested that, at least at the beginning of the grafting reaction, there is a preference to graft the DEM in the final unsaturations of the original chain, detected by means of the bands located at 992, 910 and 1642 cm^{-1} (12,13).

These previous reports could explain the results obtained here in isothermal conditions. The obtaining of T_m's after isothermal crystallization at prefixed crystallization temperatures (14), permit, in principle, the determination of the equilibrium melting temperatures, T_m^0 (Table 3) for PE samples unmodified and functionalized from the extrapolation of T_m vs. T_c, plots to $T_m = T_c$ straight line (Figure 3). This extrapolation has been frequently applied but somewhat questioned, not only in the case of ethylene α-olefin copolymers (11) and hydrogenated polybutadienes (10), but also for PE (15). The lack of general applicability results from annealing processes during heating (11). However, the extrapolation in the case of PE samples unmodified and grafted could be made, as a result of the low degree of crystallinity measured under isothermal conditions (below 20%, see Figure 1). Figure 3 shows for several functionalized samples of HDPE-4 how the extrapolation of different lines T_m vs. T_c at the line $T_m = T_c$, gives decreased values of T_m^0 with increasing grafting degree. The same tendency was found in all PE, as have been compiled in Table 3. These tendencies demonstrate, once, the homogeneous character of the grafted samples and the absence of secondary reactions that could have originated crosslinking or olefin branches different to those that the PE had originally.

When the data of $T_m°$ as a function of branch content is fitted to a straight line, a linear relationship with a slope of -2.4 is obtained. This value is smaller when compared to the prediction of the Flory equation (1) for random copolymers (i.e.,-3.5). Of such comparison it can be appreciated that the depression of $T_m°$ as a function of the fraction of molar branches is smaller than the one that would correspond to random disposition. The meaning of this comparison may indicate that grafting takes place increasing the number of branches but not in a purely random arrangement but, also, in some parts of the chain that do not promote a reduction of the crystallite size, as the one that would correspond with a random DEM distribution.

However, the results obtained from the thermal properties reflected in Figure 1, seem to confirm previous reports that indicate other possible grafting sites (16). Marquez et al., have found evidences for the grafting of DEM onto LLDPE which suggested an insertion of DEM onto secondary carbons.

Considering these two possibilities for the insertion of DEM and since the experimental evidence supports the occurrence of both, it is probable that for the HDPE and LLDPE samples modified in solution the insertion of DEM onto secondary carbons occurs, but after the initiator had consumed the terminal unsaturations. In this sense, the qualitative differences appreciated when the modification takes place in HDPE samples respect the LLDPE samples, could be explained for the presence of vinyl ends in higher proportion in the HDPE samples used in this work that in the samples of LLDPE.

Table 3. The melting peak temperature (T_m), the enthalpies of melting (ΔH_m) and the equilibrium melting temperatures (T_m^0) determined in original samples and in some of functionalized samples.

Sample	Grafted DEM (mol%)	Total branches (mol%)	T_m (°C)	ΔH_m (J/g)	T_m^0 (°C)
HDPE-1	0	0,8	126	175	139,6
HD1FUN-2	1,04	1,84	122	152	136,0
HD1FUN-9	1,59	2,39	122	144	129.6
HD1FUN-23	2,10	2,90	121	137	-----
HDPE-2	0	0,66	129	183	142,0
HD2FUN-37	0,92	1,58	126	158	139,3
HD2FUN-38	1,36	2,02	123	153	135,7
HD2FUN-39	1,55	2,21	126	150	131,5
HDPE-3	0	1,07	126	169	135,2
HD3FUN-40	0,98	2,05	122	150	135,0
HD3FUN-41	1,09	2,16	123	150	131,1
HD3FUN-42	1,63	2,70	122	138	129,5
HDPE-4	0	0,35	130	189	140,5
HD4FUN-43	1,15	1,50	125	152	135,5
HD4FUN-44	1,32	1,67	124	153	130,0
HD4FUN-45	1,59	1,94	124	155	127,5
HDPE-5	0	0,52	128	181	------
HD5FUN-48	1,67	2,19	126	138	------
LLDPE-1	0	3,40	121	113	129,0
LLD1FUN-49	1,66	5,06	116	113	122,0
LLDPE-2	0	3,80	125	122	134,0
LLD2FUN-50	1,5	5,30	119	111	128,0
LLDPE-3	0	3,90	123	112	129,6
LLD3FUN-51	1.81	5,71	118	92	125,5
LLDPE-4	0	3,20	123	125	133,3
LLD4FUN-53	1,73	4,93	118	103	127,4

Conclusions

From the thermal analysis of HDPE and LLDPE samples unmodified and grafted in solution with DEM, results were found to reach some general conclusions about the molecular architecture of the modified chains and of the reaction mechanisms that originated them.

On one side, the participant sequences in the crystallization decrease with the degree of grafting, which seems to indicate that the insertion of monomer occurs at random, that seems to confirm previous work made in LLDPE (16). On the other hand, the study of the T_m° depression indicated that, the grafting increase the number of branches but not in a purely random arrangement. This last point clarify previous evidences obtained by FTIR, respect the grafting in the terminal vinyl ends (12,13).

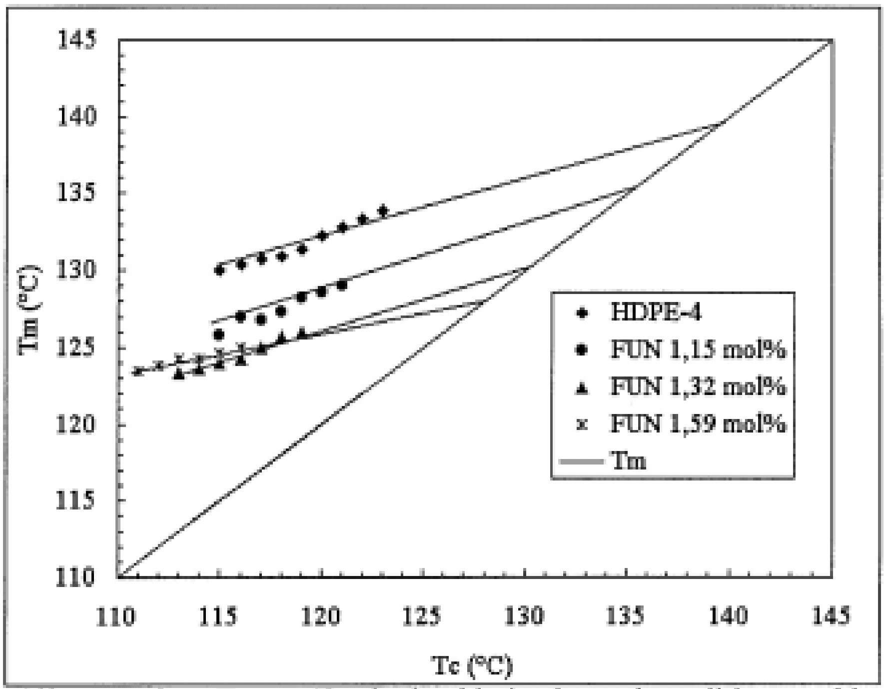

Figure 3. Different values T_m vs. T_c obtained in isothermal conditions and its extrapolation plots to $T_m = T_c$ straight line for functionalized samples of HDPE-4.

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