Solid-state nuclear magnetic resonance study of linear low-density polyethylenes: 1. Ethylene–1-butene copolymers

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The effect of crystallization conditions on the partitioning of comonomer units between crystalline and non-crystalline regions has been investigated in a copolymer of ethylene–1-butene, a linear low-density polyethylene, by using solid-state ^{13}C nuclear magnetic resonance (n.m.r.) techniques. It is shown that the cross-polarization ability of the methyl carbons in the ethyl branches is considerably lower than in the case of a hydrogenated polybutadiene taken as a model, indicating a very high degree of mobility of those branches, and resulting in the necessity for longer contact times (about 5 ms) to get a maximum in their signal. Two sample preparations (quenched and slowly crystallized from the melt, respectively) have been analysed, showing very small differences in both the n.m.r. crystallinities and the partitioning of the ethyl branches of the comonomer units. This stands in contrast with the very distinct melting patterns obtained in differential scanning calorimetry, which indicate a rather different distribution of crystallites between the two preparations. The partitioning revealed that the concentration of ethyl branches in the non-crystalline region is about five times higher than in the crystalline region for both preparations. Taking into account the crystallinity, about 9% of total branches were found to be accommodated in the crystal lattice, a number slightly higher than in the case of the model hydrogenated polybutadiene sample, but far away from the much easier inclusion of methyl branches and chain ends.

(Keywords: solid-state ^{13}C nuclear magnetic resonance; ethylene–1-butene copolymer; linear low-density polyethylene; partitioning of comonomer units)

INTRODUCTION

Linear low-density polyethylenes (LLDPE) are copolymers of ethylene and α-olefins[1] that exhibit mechanical properties quite different from those of traditional linear high-density polyethylene (HDPE) and high-pressure polymerized low-density polyethylene (LDPE). This is the basis of the increasing importance of LLDPE, with growing commercial applications.

The final properties of these polymers are very sensitive to the nature, concentration and distribution of comonomer units, as well as to the crystallization conditions. This work is part of a general study of the influence of those variables on the physical and mechanical properties of LLDPE, by analysing the correlation between the properties and the structural features imposed by the different polymerization and crystallization conditions.

One of the most important parameters governing the properties is the concentration of comonomer. However, not only is the average number of interest but also their partitioning between the crystal and amorphous phases, i.e. the possibility of incorporation of defects into the crystal. Relative to the ethyl branches, there are different points of view concerning their level of incorporation. Thus, several authors[2–4] argue that these branches should be totally excluded from the lattice under equilibrium conditions. On the contrary, other authors postulate the kinetic control[5] of crystallization from the melt, resulting in some branch incorporation. On the other hand, it has been pointed out[6–8] that more branches may be trapped in the lattice when the sample is crystallized by quenching, i.e. far from equilibrium conditions.

Recent papers have analysed this partitioning of different kinds of defects of polyethylene[9–11] by using solid-state nuclear magnetic resonance techniques. Particularly, a small amount of ethyl branches was found in crystal environments on a model hydrogenated polybutadiene (HPB), slowly crystallized from the melt[10]. These HPB are 'ideal' samples in that they have a very narrow molecular-weight distribution and the ethyl branches are randomly distributed along the chains[12].

This paper is concerned with the study of the structure of a copolymer of ethylene and 1-butene obtained with a Ziegler–Natta catalyst. The aim is to investigate the structural changes imposed by different crystallization conditions, with special emphasis on the study of the inclusion of comonomer units (bearing ethyl branches) in the crystal lattice, with the aid of solid-state n.m.r., comparing the results with the model HPB sample.

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EXPERIMENTAL

The LLDPE sample was obtained by copolymerization of ethylene and 1-butene in a high-pressure pilot-plant-scale reactor, using a Ziegler–Natta catalyst system. The characterization of molecular weight and molecular-weight distribution was carried out on a Waters ALC/GPC 150 gel permeation chromatograph at 145°C in 1,2,4-trichlorobenzene, following standard techniques. The number-average molecular weight of the sample was found to be 20000, with a polydispersity ratio $M_w/M_n = 3.61$.

Two samples of copolymer were prepared with different crystallization conditions. One of them was slowly cooled at about $2°C\,min^{-1}$, and the other was quenched into ice water. These samples were finely divided and pressed into the n.m.r. rotors.

The solid-state n.m.r. spectrometer used in this work was a Bruker MSL400, operating at 100.63 MHz, with an Oxford Instruments magnet of 9.4 T. A double-bearing MAS-DB7 probehead from Bruker was employed. The rotors were made from aluminium oxide, with poly(chlorotrifluoroethylene) end-caps. The solid-state ^{13}C n.m.r. spectra were acquired with high-power decoupling[13,14] and magic-angle sample spinning (MASS)[15,16]. The decoupler power was about 50 kHz and the spinning frequency was 4.2 kHz. Two different pulse sequences were used: one of them was the cross-polarization (CP) sequence[17,18] with various contact times, and the other was a regular 90°–5 s experiment[9,10].

The solution ^{13}C n.m.r. determination of the comonomer content was carried out on a Bruker AC300 operating at 75.47 MHz and 7.046 T. The spectrum was taken in solution in *o*-dichlorobenzene at 100°C, with the usual acquisition parameters[19].

The melting endotherms of the two sample preparations were determined on a Perkin–Elmer DSC7 differential scanning calorimeter, calibrated with different standards. The sample weight was 10–12 mg and a heating rate of $10°C\,min^{-1}$ was used. A value of $290\,J\,g^{-1}$ was taken for the enthalpy of fusion of 100% crystalline polyethylene.

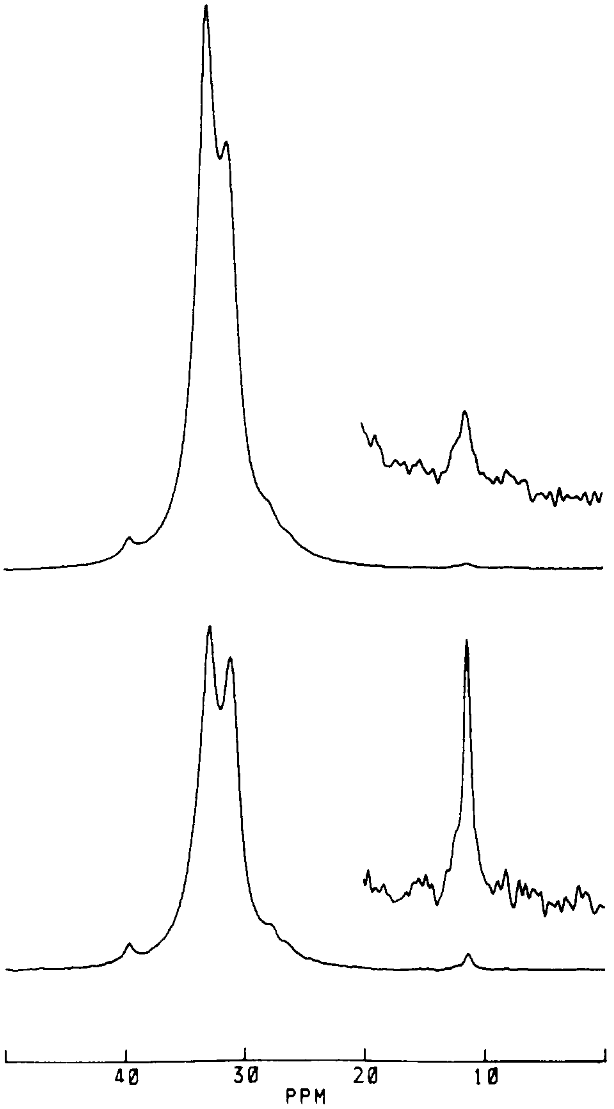
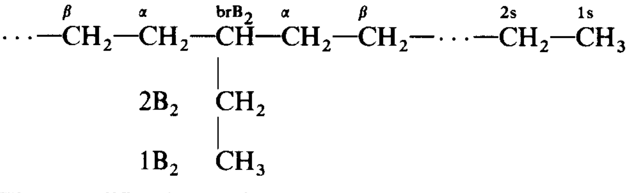


Figure 1 ^{13}C CP-MASS spectra of the LLDPE sample quenched from the melt into ice–water, acquired with two different contact times, 0.2 ms (upper) and 2.5 ms (lower), showing the methyl region amplified 16 times. The number of scans was 2500

RESULTS AND DISCUSSION

The average comonomer content of the sample and its distribution were analysed first by high-resolution n.m.r. following well established procedures[19–21]. The comonomer content was found to be 4.54 mol% of 1-butene, with a fairly random distribution of units. However, preliminary results[22] show that the comonomer is not evenly distributed along the chains, with a higher content in the lower-molecular-weight ones, a common feature of LLDPE[23–25].

On the other hand, the very different cross-polarization abilities of the ethyl branches in the two environments (crystalline and non-crystalline), and their different chemical shifts[10], were exploited to get the pure lineshapes and to obtain the partitioning of comonomer units. Thus, the CP-MASS spectra were taken for each sample, with contact times of 0.2 and 2.5 ms, respectively. *Figure 1* shows the corresponding spectra for the quenched sample. Besides the recurrent crystalline and non-crystalline methylenes at 32.9 and 31.1 ppm, other resonances associated with defect carbons can be observed in *Figure 1* at chemical shifts of 39.8, 27.9, 26.3 and 11.3 ppm. They correspond[9,10], respectively, to the carbons brB_2, β, $2B_2$ and $1B_2$ in the following scheme:



$$\begin{array}{lll} & \cdots-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-\overset{brB_2}{CH}-\overset{\alpha}{CH_2}-\overset{\beta}{CH_2}-\cdots-\overset{2s}{CH_2}-\overset{1s}{CH_3} \\ & \qquad\qquad\quad | \\ 2B_2 & \qquad\qquad\quad CH_2 \\ & \qquad\qquad\quad | \\ 1B_2 & \qquad\qquad\quad CH_3 \end{array}$$

The amplifications of the upfield regions also show a shoulder at around 12 ppm, due to the $1B_2$ carbons in the crystalline region[10]. From these amplifications, the different cross-polarization behaviours of the two $1B_2$ resonances is evident because, as was shown before[10], a higher T_{CH} for the non-crystalline $1B_2$ carbons results in the necessity for longer contact times to produce signals for that resonance with enhancement factors closer to their backbone counterparts at 31.1 ppm. (The distinct proportion of crystalline and non-crystalline backbone resonances in the two spectra of *Figure 1* is the result of the opposite influence of T_{CH} and $T^{H}_{1\rho}$, the former

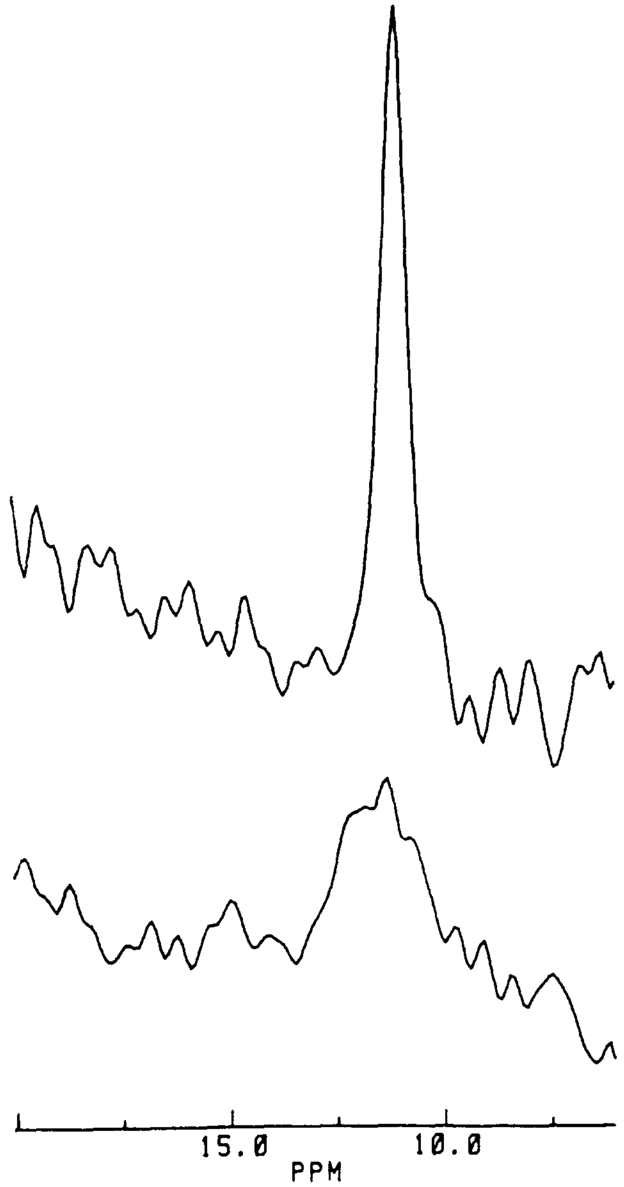


Figure 2 Pure lineshapes of the crystalline (lower) and non-crystalline (upper) methyl carbons in the ethyl branches ($1B_2$ resonance)

parameter being greater for the non-crystalline carbons, while the latter one is smaller.)

The different relative areas of the two $1B_2$ resonances can be used to obtain the crystalline and non-crystalline shapes of the pure components by the appropriate linear combinations. These shapes can be seen in *Figure 2*, and were used to obtain the areas of the components of the $1B_2$ resonance in the original spectra with a CP time of 2.5 ms. This contact time was chosen for performing the partitioning because the maximum of the non-crystalline $1B_2$ signal was found with that time for the HPB sample[10]. A similar procedure was used to deconvolute the main-chain carbon resonances. The results can be seen in *Table 1*, where the first spinning sidebands have been taken into account because they comprise a considerable area (about 5% of the total) which is mainly due to crystalline resonances. From *Table 1*, it follows that the concentration of ethyl branches is about the same for the two crystallization conditions.

On the other hand, a simple 90°–5 s experiment was acquired for each preparation of the sample, in order to calculate the true n.m.r. crystallinities, corrected for the different cross-polarization enhancement factors. (The definition of the true n.m.r. crystallinity in this paper is the proportion of carbons that resonate at 32.9 ppm, assuming a two-phase model, with the non-crystalline signal appearing at 31.1 ppm, thus neglecting the crystalline/non-crystalline interface, part of which may be included in the 32.9 ppm resonance, knowing the composite behaviour of its T_1^C decay[10].) It is well known[9,10,26,27] that in this kind of sample a 5 s delay is enough to account for all the resonances except for the crystal methylenes, whose T_1^C is of the order of 100 s. The corresponding spectra are shown in *Figure 3*, where, in addition to the resonances described above, two others can be discerned: a shoulder at about 34 ppm, corresponding to the backbone methylene adjacent to the methine, and a peak at 15 ppm, due to the methyls at the end of the chains (1 s carbons in the structure above), in analogy with the solution measurements[10,19,28–30].

Therefore, it is possible to determine the cross-polarization enhancement factors of the non-crystalline phase, ε_{NC} (as well as for the other resonances except the crystal one) by comparing the spectra in *Figure 3* with the corresponding signals in the CP experiments. This procedure gives 1.4 and 1.2 for the ε_{NC} values of the quenched and slowly crystallized samples, respectively, for a CP time of 2.5 ms. The crystalline enhancement factor, ε_C, cannot be determined from *Figure 3*, as a delay time of hundreds of seconds would be necessary to get the equilibrium crystalline signal. However, this parameter can be assumed to be equal to the one for the HPB sample mentioned before. This sample[10] gave $\varepsilon_C = 3.2$ for a CP time of 1 ms, which can be corrected with the value of $T_{1\rho}^H = 8.7$ ms[10] to give $\varepsilon_C = 2.7$ for 2.5 ms CP time. With this assumption and the apparent values in *Table 1*, the true n.m.r. crystallinities are found to be 0.32 and 0.33 for the quenched and slowly crystallized samples, respectively. These values are smaller than for the HPB sample, as they correspond to a higher comonomer content.

Knowing the true n.m.r. crystallinities, another estimation of the average concentration of comonomer can be performed from the 90°–5 s experiments in *Figure 3*, by correcting them for the missing crystalline intensity. Thus, incrementing the crystal areas from the apparent values of 14 and 15% of the total in *Figure 3* to 32 and 33% (the true crystallinities, i.e. the equilibrium values) we obtain, by integrating the whole $1B_2$ resonance, an average concentration of ethyl branches of 22.2 and 20.9 per 1000 total carbons, for the quenched and slowly crystallized samples, respectively. That corresponds to 4.5 ± 0.2 mol% of comonomer units, in perfect agreement with the solution results.

At this point, the partitioning of ethyl branches

Table 1 Areas, in arbitrary units, of the crystalline and non-crystalline components of the 2.5 ms CP experiments

Sample	Crystal area[a]	Total area	Apparent crystal content	$1B_2$ areas[b] 12 ppm	$1B_2$ areas[b] Total
Quenched	45.2	94.1	0.48	0.3	1.0
Slowly cooled	49.7	95.6	0.52	0.3	0.9

[a] Considering the spinning sidebands
[b] The error is estimated to be 0.05 units

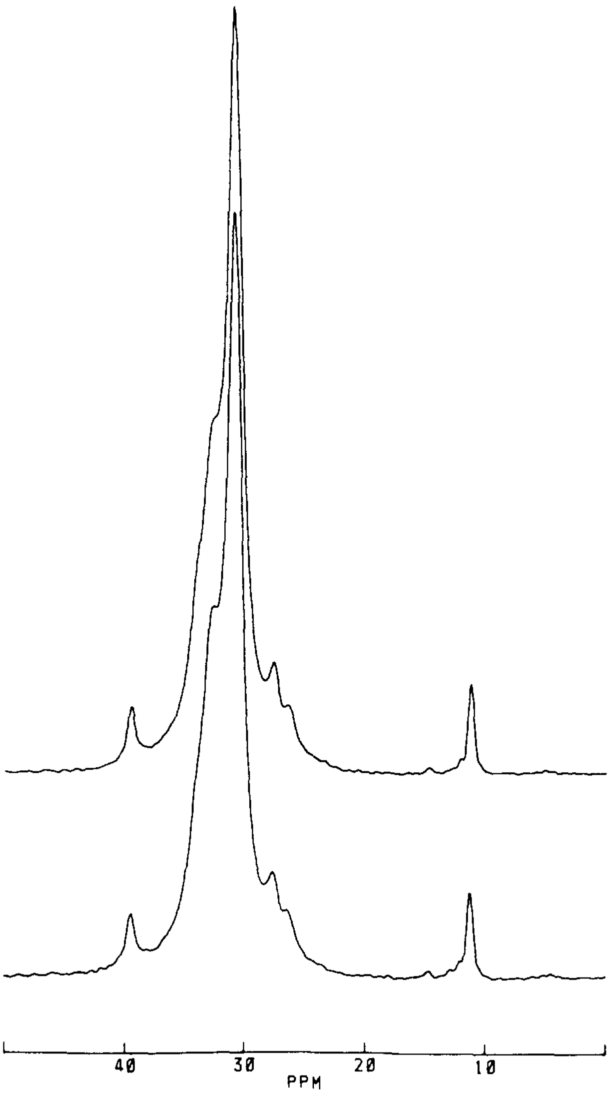


Figure 3 Solid-state ^{13}C spectra acquired with a 90°–5 s pulse sequence, corresponding to the quenched (lower) and slowly crystallized (upper) preparations of the LLDPE sample. The number of scans was 2500

between the two phases can be determined from the data in *Table 1* and the true n.m.r. crystallinities. The apparent concentrations in the crystalline and non-crystalline regions are, thus, 6.6 ± 1.1 and 14.3 ± 1.0 per 1000 total carbons in each phase for the quenched sample, and 6.0 ± 1.0 and 13.1 ± 1.1 for the slowly crystallized sample. However, having taken the crystallinities into account, the average branch content in the whole sample is then 11.8 ± 1.1 and 10.8 ± 1.1 per 1000 total carbons, for the quenched and slowly crystallized samples, respectively, far away from the real values determined either from solution or from the corrected 90°–5 s experiments.

The conclusion is, then, that even with 2.5 ms CP time we are accounting only for about 53% of the total branches, while in the HPB sample this number was 67% for just 1 ms CP time. This means that the known sluggish behaviour of the $1B_2$ resonance (the non-crystalline component) is increased in these LLDPE samples. To assess this point, a series of shorter experiments with variable CP times (up to 8 ms) was acquired for the quenched sample, and the enhancement factors were determined, by comparison with the 90°–5 s experiment. The corresponding values have been plotted in *Figure 4*, for the non-crystalline backbone and $1B_2$ carbons. It can be seen that 1 ms is enough to get a maximum efficiency for the backbone resonance, while even more than 5 ms is necessary to account for the $1B_2$ carbons, when an important part of the signal is already missed by $T^{H}_{1\rho}$ relaxation. The value of this relaxation time for the non-crystalline resonance can be determined to be 5.2 ms from the slope of the decay.

Therefore, the value of $\varepsilon = 0.8$ for the non-crystalline $1B_2$ carbons for 2.5 ms CP time, compared with 1.4 for the corresponding backbone resonance, can explain why a very low number was obtained for the average concentration of branches from the CP experiments. Thus, the best way to determine the partitioning is to suppose that the crystal $1B_2$ carbons are well accounted for with 2.5 ms and to calculate the non-crystalline ones by taking the difference from the known average concentration in the sample. This assumption leads to a concentration of branches that is 6.6 ± 1.1 and 28.5 ± 1.5 per 1000 carbons in the crystalline and amorphous phases, respectively, of the quenched sample, and 6.0 ± 1.0 and 29.1 ± 1.5 for the slowly crystallized sample. Therefore, although these values seem to indicate a slightly higher concentration of branches in the crystal for the quenched sample, the difference is well inside the experimental error. It is clear, however, that the concentration of branches is about five times higher in the non-crystalline phase, while about $9 \pm 2\%$ of all branches are found in crystalline environments. This percentage is in agreement with the shoulder at 12 ppm, which can be seen in the 90°–5 s experiments, but it is more difficult to deconvolute that signal in these spectra because of the

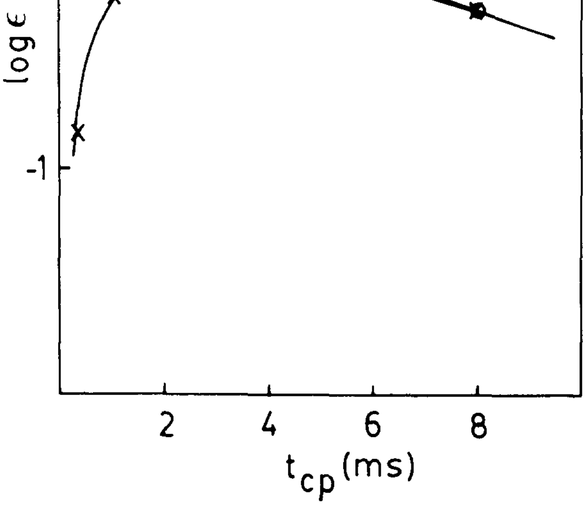


Figure 4 CP enhancement factors of non-crystalline components as a function of the contact time, corresponding to the quenched LLDPE sample: (o) backbone carbons; (x) methyl carbons in the ethyl branches ($1B_2$ resonance)

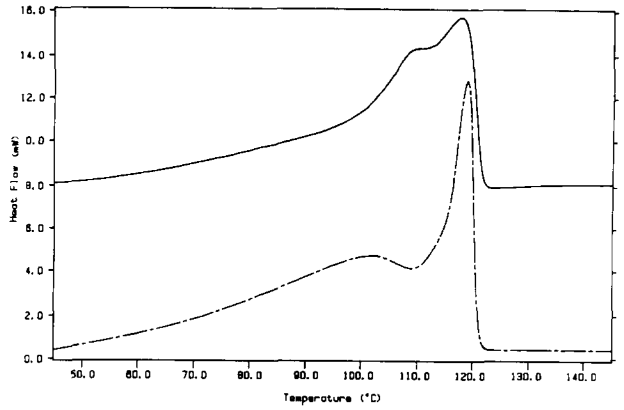


Figure 5 D.s.c. traces of the quenched (upper) and slowly crystallized (lower) preparations of the LLDPE sample (heating rate, 10°C min^{-1})

much higher proportion of the non-crystalline component.

The first main conclusion derived from this work is, then, that the cross-polarization ability of the ethyl branches in the LLDPE sample is substantially worse than for the HPB sample[10]. This indicates the existence of a very high mobility of the non-crystalline ethyl branches, causing a reduction of proton–carbon dipolar fields with the subsequent lowering of the CP efficiency of these carbons relative to the non-crystalline backbone ones. (A higher mobility can also be deduced for the non-crystalline and even for the crystalline backbone carbons when compared to high-density polyethylene, with enhancement factors considerably greater[31] than these copolymers.) We believe that the difference between LLDPE and HPB is due not only to the higher comonomer content but also to the known higher dispersity of branches in the former sample, with a greater concentration in the lower molecular weights. The same arguments may apply for the higher concentration of branches in crystalline environments. Nevertheless, the percentage of branches in the crystalline phase is only 9%, far away from the much easier inclusion in the crystal of methyl branches and chain ends[11], indicating that the ethyl branches could be totally excluded from the lattice under equilibrium crystallization conditions.

The second conclusion is that the change in crystallization conditions for the LLDPE samples studied here seems to have a minor effect, judging from the solid-state n.m.r. results of crystallinities and partitioning of comonomer units. However, there is an evident difference in the corresponding d.s.c. thermograms, as can be seen in *Figure 5*. The pattern for the quenched sample suggests the existence of more imperfect crystals, but that can be due to smaller crystal thicknesses or also to the crystallization of segments with a different content or distribution of comonomer units[2]. More work needs to be done to clarify this point, because the dispersity of molecular weight and branch distribution may lead to different results than for HPB samples. Nevertheless, it seems clear that the two crystallization conditions used here have little effect on the crystallinity of this LLDPE sample, because the enthalpies of fusion derived from *Figure 5* are very similar. The crystallinities calculated from these enthalpies are 34 and 38% for the quenched and slowly crystallized samples, respectively (with an estimated error of about 3%), in good agreement with the n.m.r. results.

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