

# Dynamic Mechanical Properties of Low-Density and Linear Low-Density Polyethylenes. Influence of Molecular Segregation

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## Synopsis

The dynamic mechanical properties of different low-density and linear low-density polyethylenes have been measured as a function of crystallization conditions. The mechanical results have been explained accounting for molecular segregation as well as reorganization capacity of the crystallizable segments during isothermal thickening. The presence of a high amount of segregated material does not allow detection of any relationship between crystallization conditions and mechanical relaxations for three of the four samples. The average values of the resonance relaxation temperatures and the relaxation strengths are dependent on branch content and branch type.

## INTRODUCTION

Polyethylene (linear and branched) displays three well-known relaxations in isochronal dynamic mechanical experiments: the alpha, beta, and gamma relaxations.<sup>1-3</sup> The alpha relaxation process is thought to be due to deformation movements into the amorphous region as a consequence of reorientations within the crystallites<sup>4</sup> and usually ranges from 303 to 340 K. The beta relaxation appears in the temperature range 233–253 K and has been recently assigned to the relaxation of chain units located in the interfacial region.<sup>5</sup> Finally, the gamma relaxation, which is observed in the temperature range 148–173 K, has been interpreted as the consequence of low activation energy conformational reorientations of three, five, or more chain units of the main backbone known as crankshaft movements.<sup>6,7</sup>

In a recent article published by the authors, a study covering the influence of crystallization conditions on the dynamic mechanical properties of four different high-density polyethylene samples was reported.<sup>8</sup> Among its several conclusions, this study highlights the important role played by molecular segregation in the dynamic mechanical spectra of these samples. Molecular segregation<sup>9-13</sup> is a concept that accounts for the separation during crystallization of molecules less favored from a thermodynamic standpoint (low molecular weight specimens or highly branched chains). This rejection of the less favored chains gives rise to two different crystallization paths: one isothermal

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and one nonisothermal. When the amount of rejected material approaches a critical value, the reorganization factor, measured by infrared spectroscopy, as well as the dynamic mechanical properties become insensitive to the structural changes that take place during isothermal thickening due to the averaging character of these two techniques.

This study aims to determine the influence of molecular segregation in branched samples, i.e., low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE). The LDPE samples are characterized by the presence of several different types of branches on their structure, *n*-butyl, *n*-amyl, and long branches being the most important,<sup>14</sup> while the LLDPE samples studied herein are hexyl branched (copolymers of ethylene and 1-octene).

## EXPERIMENTAL

### Materials

The molecular features of the four branched samples studied in this work have been summarized in Table I. The headings in this table refer to the number and weight average molecular weights ( $M_n$  and  $M_w$ , respectively), the density of the samples, the number of CH<sub>3</sub> groups per 1000 CH<sub>2</sub> units, and the mean distance between branches defined in Ref. 8. The isothermal treatment was carried out in an oven with a temperature control better than  $\pm 0.4$  K. Prior to the isothermal treatment each sample was compression molded in a laboratory press at 423 K for 5 min. Different crystallization conditions have been programmed in the oven in order to characterize the behavior of the samples on isothermal thickening.

### Differential Thermal Analysis (DTA)

The DTA instrument, a Mettler TA-2000, was calibrated according to standard procedures. The melting endotherms were recorded at a scan rate of 10 K/min.

TABLE I  
Molecular Features of the Polyethylene Samples

Sample code	$M_w^a$ (g/mol)	$M_n^a$ (g/mol)	Dens <sup>a</sup> (g/cc)	CH <sub>3</sub> /1000 CH <sub>2</sub> <sup>b</sup>	$\langle l \rangle^c$
8065 <sup>d</sup>	63,000	21,000	0.965	< 1	2370
4255 <sup>d</sup>	72,000	21,000	0.955	5	671
2505 <sup>d</sup>	44,000	15,000	0.955	5	671
4005 <sup>d</sup>	40,000	11,500	0.950	16	180
585 <sup>e</sup>	70,000	12,500	0.922	21	143
149 <sup>e</sup>	115,000	21,000	0.919	31	106
2049 <sup>f</sup>	107,000	27,000	0.926	11	276
XZ-07 <sup>f</sup>	128,000	31,500	0.905	26	116

<sup>a</sup> Provided by the supplier.

<sup>b</sup> By infrared spectroscopy (see Ref. 22).

<sup>c</sup> Values obtained by means of eq. (3) in Ref. 8. This magnitude refers to the mean distance between branches considering extended chains and total segregation of the imperfections.

<sup>d</sup> The dynamic mechanical study of these samples has already been reported in Ref. 8.

<sup>e</sup> Low-density polyethylenes.

<sup>f</sup> Linear low-density polyethylenes.

Samples weighing from 5 to 10 mg were cooled in the DTA instrument from 423 K to the programmed crystallization temperature at a rate of 20 K/min. After the crystallization took place, each sample was quenched in ice water. Once the sample has been cooled, the melting corresponding to the studied thermal history was recorded. All crystallinity determinations are based on a value of 293 kJ/kg as the heat of fusion of 100% crystalline polyethylene.<sup>15</sup>

### Infrared Spectroscopy

The structural study has been carried out by means of a Mattson Instruments Fourier transform infrared spectrophotometer (model Polaris Icon) provided with a DTGS detector and a dry air installation. The films were prepared by compression molding with a mean thickness of 200  $\mu\text{m}$ . Spectra were obtained after 125 scans at a resolution of 2  $\text{cm}^{-1}$ .

The assignment of the bands has been undertaken according to Krim<sup>16</sup> and Snyder.<sup>17</sup> The infrared study has been focused on the polyethylene wagging spectral region mainly in the peak at 1368  $\text{cm}^{-1}$  assigned to the  $\text{CH}_2$  wagging mode in GTG and GTG' conformations, which is very sensitive to conformational changes.<sup>8,18</sup>

For the sake of comparison, the reduced structure factor (RSF) of the band at 1368  $\text{cm}^{-1}$  has been calculated. This structural factor can be defined according to the following equation:

$$\text{RSF} = A_{1368}/A_{909}$$

where  $A_{1368}$  and  $A_{909}$  are the absorbances of the bands at 1368 and 909  $\text{cm}^{-1}$  (this being associated with the wagging vibration of end  $\text{CH}=\text{CH}_2$  groups.<sup>19</sup> The RSF is independent of the changes in crystallinity and thickness of the samples.<sup>20,21</sup> It is also interesting to define, as we did previously,<sup>8</sup> the reorganization factor,  $R_x$ , as the ratio between the RSF at  $x$   $\text{cm}^{-1}$  of the isothermally crystallized sample and the RSF at the same wave number of the air-quenched sample. The value of the reorganization factor, therefore, will vary between 0 and 1, corresponding the first case to an extended chain equilibrium crystal and the second one to the quenched sample.

The methyl group concentration has been calculated by infrared spectroscopy on quenched films using the equation by Bryant and Voter.<sup>22</sup> Better resolution of the peak at 1377  $\text{cm}^{-1}$  (assigned to the methyl group) has been achieved by subtraction of the spectrum of a linear polyethylene displaying similar molecular weight features to our materials from our sample spectra making zero the peak at 1368  $\text{cm}^{-1}$ .

### Dynamic Mechanical Thermal Analysis (DMTA)

The mechanical analysis was performed in a Polymer Laboratories DMTA apparatus interfaced to a Hewlett-Packard computer. The mechanical mode used was the bending one, sharp knife-like supported.<sup>23</sup> All of the samples were run according to the following instrumental conditions: a scan rate of 3 K/min, a frequency of 1 Hz, and a temperature range from 133 to 403 K. The samples for this analysis were prepared as previously stated. The mean dimensions for the samples between the clamps were 10  $\times$  40  $\times$  0.65 mm.

The transition temperatures were more accurately determined by calculation of the first derivative of the mechanical spectra using a computer program based on the five-points parable method.

## RESULTS AND DISCUSSION

As in the previous work on high-density polyethylenes reported by the authors,<sup>8</sup> calorimetric and spectroscopic results are first presented to aid the understanding of the dynamic mechanical results.

### Degree of Segregation and Kinetic Properties

Due to the branched nature of these samples, it must be expected they will present a high degree of segregation. Figure 1 shows the change in the percentage of segregated material as a function of crystallization temperature. The relevant aspects of this figure follow.

1. The two LDPE samples behave in a similar manner independently of their molecular weight and branch content (see table I). The amount of segregated material is fairly constant for low crystallization temperatures and, from 370 K, it grows steeply.
2. For the LLDPE samples, the molecular features do affect the conduct of

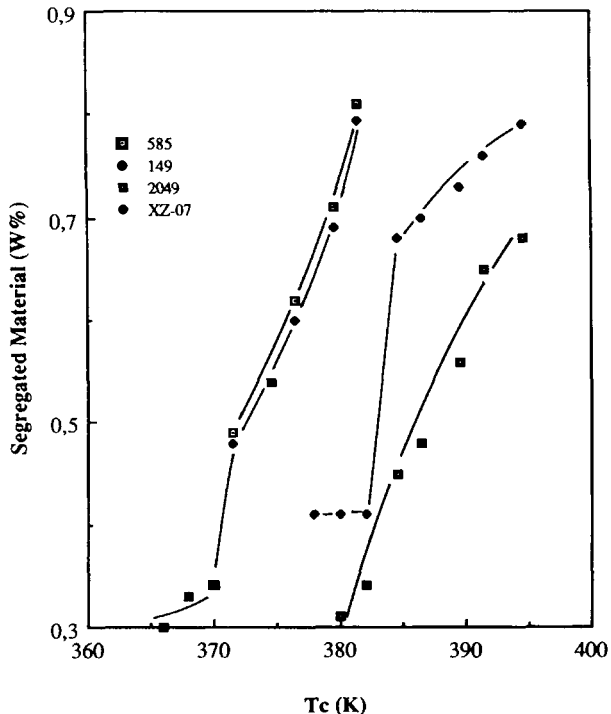


Fig. 1. Variation of the percentage of segregated material as a function of crystallization temperature.

both samples. While the highly branched sample XZ-07 presents a similar plateau area to that observed in the LDPE samples for low crystallization temperatures, for the sample 2049, the amount of segregated material increases steeply all over the crystallization temperature range studied. The percentage of segregated material, moreover, is higher for the more branched sample than for the other one for all the temperatures.

3. The influence of the type of branch becomes apparent from this plot. The long branches (more than six methylene units) present in the LDPE samples give rise to an important shift of the temperature range where crystallization takes place. Moreover, the profile found for all these samples suggests the presence of a wide distribution of crystallizable segments between branch points.

The analysis of the previous plot allows us to propose the existence of two different regions of crystallization. In the first region (plateau region), the crystallization of the highly crystallizable molecules promotes the subsequent crystallization of other segments not so favored from a thermodynamic viewpoint following an epitaxial growth type. This type of crystallization explains the small changes in the amount of segregated material with changes in the crystallization temperatures. In the second region, however, only the thermodynamically favored material (segments of enough length) is able to crystallize at each temperature.

The influence of the type of branch aforementioned becomes also apparent from the analysis of the kinetics properties. Figure 2 shows the change in the inverse of the logarithm of the semicrystallization time as a function of crystallization temperature. For the sake of comparison, the results found for a high-density highly linear polyethylene sample<sup>8</sup> have been represented together with the results found for the branched samples. The most striking aspects arising from this figure follow.

1. As expected, the higher branch content of the sample XZ-07 brings about larger crystallization rates for the same crystallization temperature than for 2049. However, the observed change is not as big as the results on the HDPE samples suggest.<sup>8</sup>
2. The long character of the branches of the LDPE samples gives rise to a shift of the crystallization range toward lower temperatures. In spite of the differences in molecular weight and branch content (see Table I), the kinetic behavior is equal, within the experimental error, for both samples. This can be due to a self-canceling effect of both variables: the lower molecular weight corresponds to the less branched sample.
3. The four samples display two slopes that may correspond to two different crystallization regimes,<sup>24</sup> although the presence of two different slopes without changes in the morphology of the samples (LLDPE ones) have been reported by Rego and Gedde in a recent paper.<sup>25</sup>

Herein we will not proceed to the application of the nucleation theory by Hoffman and collaborators<sup>24</sup> as we did in the preceding study<sup>8</sup> due to the little relevance of the knowledge of the fold surface free energy in the discussion of

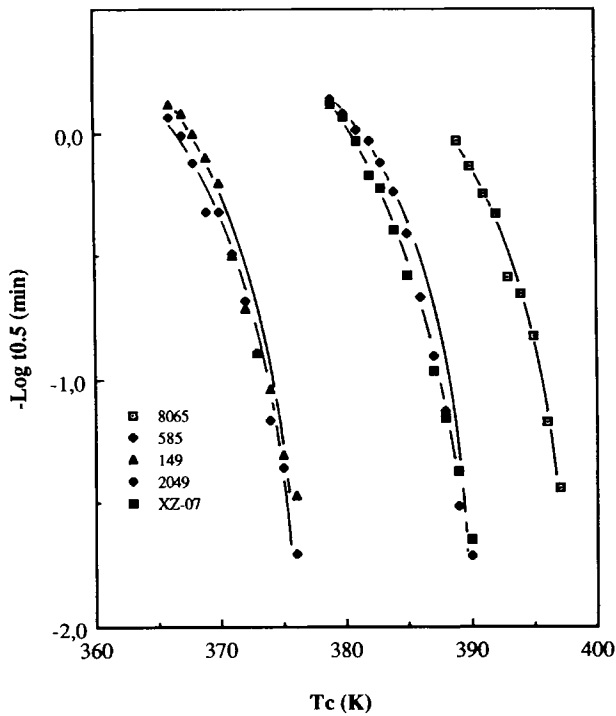


Fig. 2. Inverse of the logarithm of the semicrystallization time as a function of crystallization temperature.

the dynamic mechanical properties. At this point it is important to underline that all the infrared and dynamic mechanical measurements have been carried out in the region of low crystallization rate in order to prevent nonisothermal crystallization.

### Reorganization Factor

The analysis of the infrared data (this time only focused on the peak at  $1368\text{ cm}^{-1}$  corresponding to the wagging vibration of methylene units within *gtg* and *gtg'* sequences) provides no reliable data for samples 2049 and 149 due to the low absorbance of the peak at  $909\text{ cm}^{-1}$ , which gives rise to important errors in the determination of the reorganization factor. The results obtained for the other two samples are shown in Figure 3 [Fig. 3(a) is LDPE 149 and Fig. 3(b) is LLDPE XZ-07]. There are two remarkable aspects arising from this figure.

1. As in the case of the HDPE samples, the reorganization factor for the isothermally thickened samples is always less than one.
2. Both samples, however, display reorganization factor values very close to one all over the crystallization temperature and time ranges studied.

This last observation is due to the large amount of segregated material for all these samples, which does not allow for quantitative evaluation of the capa-

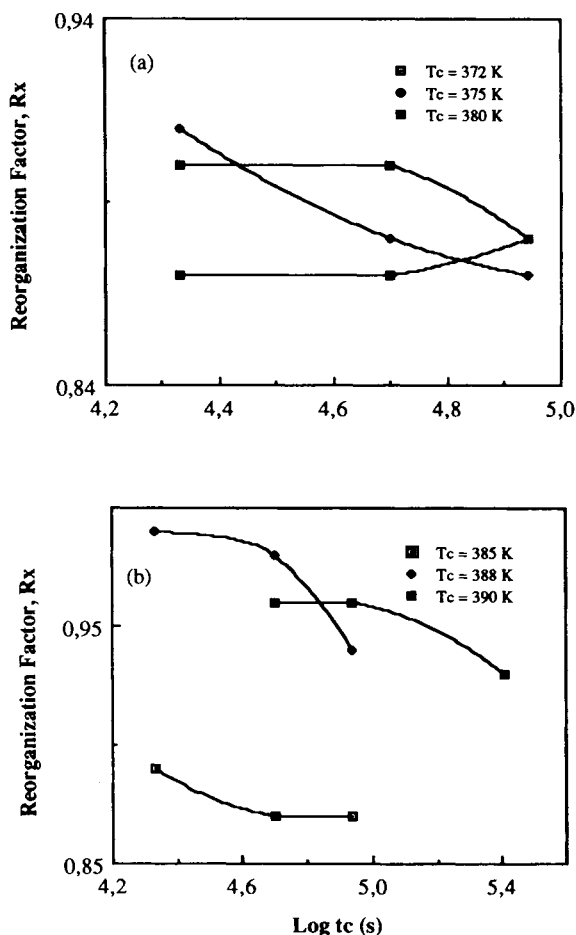


Fig. 3. Variation of the reorganization factor,  $R_x$ , as a function of crystallization temperature and time. (a) Material 585, (b) material XZ-07.

bilities of the system to decrease the thickness of the amorphous layer on isothermal thickening.

The well-known representation of melting point as a function of crystallization temperature, on the other hand, provides some insight about the capabilities of the four different polyethylenes for reorganization on isothermal treatment (Fig. 4). It is apparent from this figure that the highest slope corresponds to sample 2049, which displays the least branch content. The higher the branch content, the smaller the mean length between branches, thus implying a reduced capacity of the sample to increase its crystalline thickness on isothermal treatment and, therefore, a small variation of the melting point with crystallization conditions. This behavior for these branched samples agrees with the conclusions drawn from the reorganization factor calculation aforementioned, that is, the more branched samples tend to keep constant their crystalline thickness independently of the thermal history (sample 2049 does not fit this behavior).

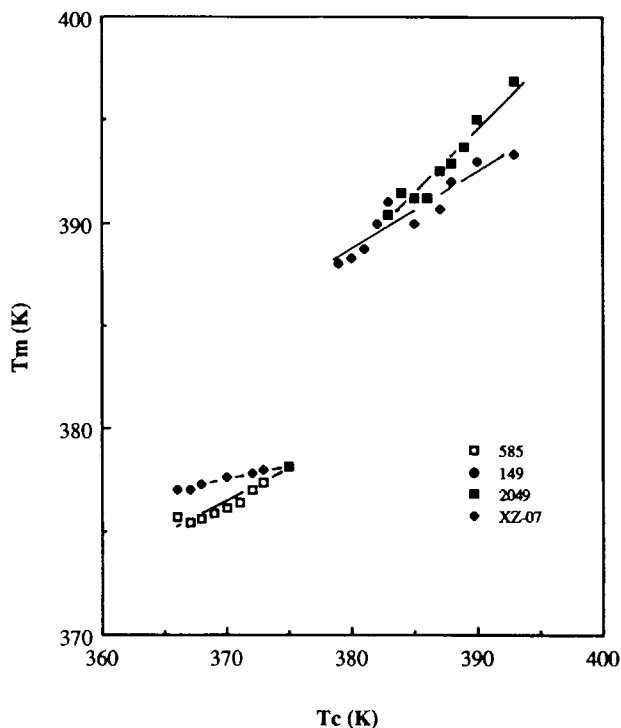


Fig. 4. Melting point versus crystallization temperature.

### Dynamic Mechanical Behavior

As a consequence of the high interferences due to the segregated material observed in the infrared study, we could expect the same problem for the dynamic mechanical properties measurements: the incapability to find any relationship between these mechanical properties and crystallization conditions. This is true for all of the samples except for the LLDPE 2049, which displays a similar behavior to that found for HDPE and reported elsewhere,<sup>8</sup> that is, a change in the alpha relaxation depending on crystallization conditions (Fig. 5). For low crystallization temperatures, the values found for the resonance temperature of the alpha relaxation are similar to that for the air-quenched sample (298 K). As long as the crystallization temperature is higher, the melting point (Fig. 4) and the alpha relaxation temperature increase. This tendency breaks for a given crystallization temperature (391.7 K), for which, in spite of the higher melting point displayed by the sample, the alpha relaxation temperature decreases as a consequence of the increment in the amount of segregated material (Fig. 1). Due to the character of the dynamic mechanical measurements, the spectra represent only mean values of overall relaxations taking place in the system. This, together with the low-strength character of the relaxation itself due to the presence of branches, makes it difficult to discern among the relaxations corresponding to each lamellar thickness. In this case, moreover, we have not been able to detect any asymmetry in the gaussian peak, which in our previous work we assigned to a lamellar thickness distribution.



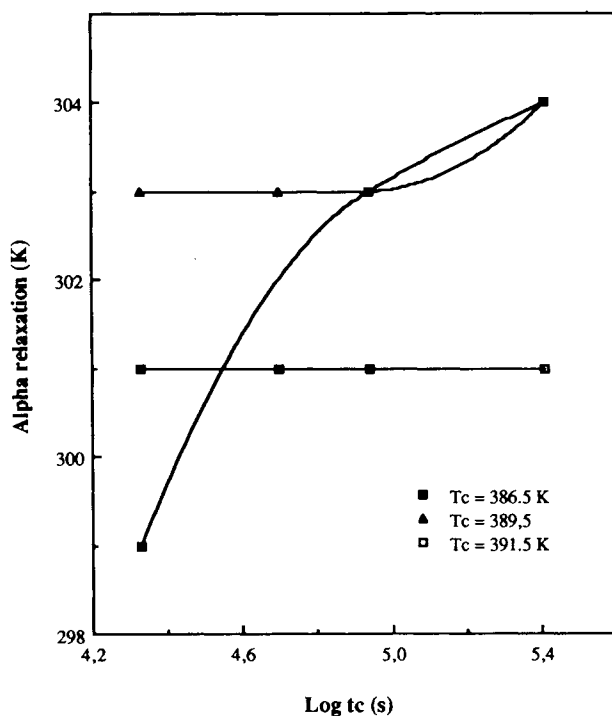


Fig. 5. Alpha relaxation temperature as a function of crystallization temperature.

The other three branched samples do not present any salient change in the alpha relaxation as a function of crystallization temperature and crystallization times due to the low value of the mean length between branches, which does not allow the chains to reorganize on isothermal thickening. However, the average values of the resonance relaxation temperatures as well as their strengths (obtained over 25 measurements for each polymer) (Table II) present an interesting behavior. For the sake of comparison, the data obtained for the HDPE

TABLE II  
Average Dynamic Mechanical Properties of the Polyethylene Samples

Sample code	Total <sup>a</sup> crystal.	$\langle T_{\alpha} \rangle$ (K)	$\langle T_{\beta} \rangle$ (K)	$\langle T_{\gamma} \rangle$ (K)	$\langle \sin \delta \rangle_{\alpha}$	$\langle \sin \delta \rangle_{\beta}$	$\langle \sin \delta \rangle_{\gamma}$	$\langle \sin \delta \rangle_{\alpha} / \langle \sin \delta \rangle_{\beta}$
8065 <sup>b</sup>	86	325	237	167	0.162	0.042	0.046	3.86
4255 <sup>b</sup>	75	319	250	167	0.139	0.036	0.045	3.86
2505 <sup>b</sup>	72	315	251	165	0.146	0.041	0.045	3.56
4005 <sup>b</sup>	68	309	252	162	0.124	0.037	0.043	3.35
585	46	291	251	150	0.130	0.077	0.041	1.69
149	45	290	250	151	0.136	0.081	0.041	1.68
2049	50	300	251	161	0.123	0.067	0.046	1.84
XZ-07	33	295	235	154	0.156	0.090	0.0476	1.73

<sup>a</sup> See experimental part and Ref. 12.

<sup>b</sup> Data reported in Ref. 8.

samples, which have been already reported,<sup>8</sup> have also been included in this table.

We will comment on the most salient features arising from Table II taking each relaxation as a separate item.

**1. Alpha Relaxation.** The transition temperatures are functions of the segmental mean length between branches,  $\langle l \rangle$  (see Table I), for the high-density samples and the linear low-density ones. The low-density polyethylenes have relaxation temperatures independent of  $\langle l \rangle$ . For similar branch contents, the resonance temperature is determined by the type of branch. This is the case for samples 4005 and 2049 and XZ-07 and 585. Sample 4005, which has a higher branch content than sample 2049 (within the experimental error due to the method used for the estimation of this branch content), displays also a higher alpha resonance temperature, probably as a consequence of the nature of the branch (short branches in high-density polyethylene and hexyl branches in linear low-density polyethylenes). Sample 585 shows lower branch content than XZ-07 and also lower relaxation temperature, again due to the nature of the branches: the presence of a certain concentration of long branches in low-density polyethylene (higher than six methylene units)<sup>14</sup> and hexyl branches in linear low-density polyethylene. The decrease in the resonance temperature with increasing branch content and branch length finds an explanation in the molecular interpretation by Boyd<sup>4</sup>: the rejection of the branches during the crystallization process leads to a more loosely organized amorphous fraction as well as a thicker amorphous intercrystalline layer. Thus, on translational mobility of the crystal occurring during the alpha process, the interface does not reorganize through changes in the loop length, and it goes through rotational and translational movements of the chains within the thick amorphous layer. This brings about a decrease in the resonance relaxation temperature.

Regarding the relaxation strength, represented herein as the  $\langle \sin \delta \rangle$  for the peak, it is easy to find out that these values are only apparent due to the influence of the neighboring beta relaxation on the strengths. To prevent this influence, we have calculated the ratio between the strengths of the alpha relaxation and the strengths of the beta ones. The results are also given in Table II. From these values it is clear that, within the experimental error, the strength of this relaxation depends on branch content and type of branch. The low value of this ratio found for sample 2049 confirms this conclusion: in spite of the lower branch content measured for this sample compared to HDPE sample 4005, it displays a lower value of the ratio, which indicates lower relaxation strength.

**2. Beta Relaxation.** Except for samples 8065 and XZ-07, the beta relaxation appears at a fairly constant temperature of 251 K, independent of branch content, branch type, crystallinity, and mean lamellar thickness. Accounting for the molecular interpretation given by Boyd,<sup>4</sup> the values found for samples 8065 and XZ-07 represent, at least, a point for speculation. The highly linear character of sample 8065 brings about a beta relaxation rather diffuse and difficult to resolve from the neighboring

gamma and alpha relaxations.<sup>4</sup> This implies a large error in the determination of the resonance temperature and, thus, no definitive conclusions can be drawn from the value found for this polymer. Sample XZ-07, on the other hand, displays a very well defined beta transition. The low value of the beta peak for this sample compared to the others might be explained accounting for the iso-free volume character of this relaxation (as a glass transition), for the reinforcing effect due to the crystalline phase, and for the region where the movements take place (the intercrystalline zone).<sup>26</sup> If the overall crystallinity decreases, the intercrystalline region as well as the free volume content become bigger, giving rise to the decrease of the beta relaxation temperature.

The relaxation strength for the beta relaxation, on the other hand, correlates well with crystallinity as pointed out by Boyd<sup>27</sup>: as long as the crystallinity decreases, the relaxation strength increases.

- 3. Gamma Relaxation.** Within the series of the high-density polyethylenes and hexyl-branched polyethylenes, the resonance temperature for this relaxation decreases with increasing branch content, while it remains constant for the low-density polyethylenes. Moreover, these LDPE samples display the lowest value compared to the HDPE and LLDPE ones. Thus, the crankshaft motion, proposed to be the molecular interpretation for this relaxation,<sup>4</sup> seems to be favored when the amorphous content is higher, probably due to the less constrained character of the amorphous layer in this case.

Regarding the relaxation strength, it remains fairly constant all over the studied samples independently of the structural features aforementioned.

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