

Determination of the Influence of Structure and Thermal History on the Dynamic Mechanical Properties of High Density Polyethylenes

J. M. REGO,* J. A. GONZALEZ OROZCO, and ISSA KATIME,[†] *Grupo de Nuevos Materiales, Departamento de Quimica-Fisica, Facultad de Ciencias, Universidad del Pais Vasco, Apartado 644, Bilbao, Spain*

Synopsis

This work is aimed at determining the influence of molecular weight distribution, branch content, and thermal history on the dynamic mechanical properties of four high density polyethylenes. Molecular segregation as a function of crystallization conditions has been measured by means of differential thermal analysis, whereas infrared spectroscopy allowed us to relate the structural changes introduced by the use of different crystallization conditions with both molecular segregation and dynamic mechanical properties. The α -relaxation is the most affected transition by thermal treatments. Molecular segregation plays an important role in the mechanical behavior when the amount of segregated material is big enough as to shield the effect due to the isothermally thickened crystals. The presence of a high degree of segregation brings about asymmetry in the α -relaxation peak as well as detectable changes in the reorganization factor (which defines the degree of order within the system) obtained by infrared spectroscopy. The supermolecular structure is found not to affect the dynamic mechanical properties. The β -relaxation depends on the branch content, whereas the γ -relaxation remains constant regardless of structural characteristics and thermal conditions.

INTRODUCTION

The isochronal mechanical spectrum of high density polyethylene. (HDPE) displays three major relaxations, the assignment of which represents, at least, a source of discussion.¹⁻³ As a general rule, the high temperature transition (α transition) is commonly considered to be related with relaxations which occur in the crystalline phase, while the β and γ transitions are related to the amorphous and interfacial region.³

The γ -relaxation is observed in the temperature range 148–173 K and is often considered as a subglass transition arising as a single process in the amorphous phase.³ Sillescu, Spiess, and co-workers,⁴⁻⁶ by determining the deuterium quadrupole resonance in linear polyethylene (LPE), have interpreted the mechanical spectrum in this region as the consequence of low activation energy conformational reorientations of three, five, or more chain units of the main backbone known as crankshaft movements.^{7,8}

* Present Address: Dpt. Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England.

[†] To whom all correspondence should be addressed.

The β -relaxation appears in the temperature range 233–253 K. This relaxation was associated with processes occurring in the amorphous phase, mainly Brownian type movements as well as relaxation of side groups and short branch points.⁹ Boyer¹⁰ and Simha and Enns,¹¹ by performing calorimetric studies on amorphous polyethylene, produced by rapid quenching, identified this transition with a glass–rubber transition. Davis and Eby¹² suggested the same assignment after studying the time dependence of volume relaxation in this region in LPE. They found that this transition had the WLF behavior characteristic of a glass–rubber transition. Popli and Mandelkern¹³ from ¹³C-NMR measurements of time correlation found values too low values of this magnitude in the β as to be considered a glass–rubber transition. Finally, Mandelkern and co-workers,¹⁴ analyzing the interfacial content by Raman spectroscopy, put forward that the β transition is a consequence of the relaxation of chain units located in the interfacial region.

The α process usually ranges from 303 to 340 K. The position and strength of this relaxation have been generally associated with crystal thickness¹⁵ and crystallinity level,¹⁶ respectively. However, Mandelkern and co-workers¹⁴ have pointed out that the level of crystallinity and supramolecular structure play no significant role in the mechanism of this relaxation and that this transition is determined mainly by the fold period. On the other hand, Boyd,¹⁷ after analyzing the relaxation behavior of *n*-paraffins, concluded that the mechanism responsible for this transition involved deformation movements within the amorphous regions due to reorientations within the crystallites.

An important reported observation is the apparition of two relaxations in the representation of the loss modulus (E'') as a function of $1/T$ (T is the absolute temperature) which has been interpreted by Nagou et al.¹⁵ as the result of two types of relaxation mechanisms: one associated with the defect region within the crystalline region and the other one associated with the amorphous region. Popli et al.¹⁴ have put forward an explanation based on the existence of a lamellar thickness distribution.

The aforementioned studies, carried out in order to develop a better understanding of the complex relaxation behavior of semicrystalline polymers, do not account for a basic phenomenon found in this kind of materials: molecular segregation.^{18–22} When isothermal studies are performed in polyethylene, one of the most important variables to be controlled is the separation during crystallization of molecules less favored from a thermodynamic standpoint (low molecular weight species or highly branched chains), which gives rise to two different crystallization paths: an isothermal one which involves those molecules able to crystallize (with a molecular weight higher than the critical one or with a chain length between branches large enough as to get stabilized in the crystalline phase at the crystallization temperature) and a nonisothermal crystallization of those molecules, not included in the first path, that crystallize upon further cooling.

This study is aimed at relating changes in the relaxation spectra of high density polyethylenes with the presence of molecular segregation. The strategy for obtaining fruitful information has been to vary the different variables affecting the molecular segregation, mainly crystallization temperature and crystallization time, over the widest range of possibilities. The fraction of segregated material has been determined by means of differential thermal analysis (DTA),

while the structural changes associated with the thermal history have been analyzed by Fourier transform infrared spectroscopy (FTIR).

EXPERIMENTAL

Materials. The molecular characteristics of the materials used in this work are summarized in Table I. The samples were subjected to isothermal and non-isothermal treatments. The isothermal treatment was carried out in an oven with a temperature control better than + 0.4 K. Prior to the isothermal treatment each sample was compression moulded in a laboratory press at 423 K for 5 min. Different crystallization conditions were 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.

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 had been cooled, the melting behavior corresponding to the appropriate thermal history was recorded. All crystallinity determination are based on a value of 293 kJ/kg as the heat of fusion of 100% crystalline polyethylene.¹⁹ The crystallization data was treated according to the following equation^{22,23}:

$$1/t_{(0.5)} = C \exp[-U^*/RT(T - T_\infty)] \exp[-K_b \sigma_e T_M^0 / (k \Delta h_f T \Delta T f)] \quad (1)$$

where $t_{(0.5)}$ is the time at which 50% of the final crystallinity is obtained, U^* is the activation energy for short range transport of crystallizable units, T_∞ is a temperature related with the glass transition, k is a constant integer which is either 2 (regime II of crystallization) or 4 (regime I), b is the monolayer thickness, σ is the lateral surface free energy, σ_e is the fold surface free energy, T_M^0 is the equilibrium melting temperature, Δh_f is the heat of fusion, ΔT is the supercooling, f is a correction factor which accounts for changes in Δh_f with temperature and equals $2T/(T_M^0 + T)$, T is the crystallization temperature, and C is a constant.

TABLE I
Molecular Characteristics of the High Density Polyethylene Fractions

Polymer	M_w^a	M_n^a	Density (g/cc) ^b	% CH ₃ /1000 CH ₂ ^c
8065	63,000	15,000	0.965	< 1
4255	72,000	21,000	0.955	5
2505	40,000	15,000	0.955	5
4005	40,000	11,500	0.955	16

^a By GPC.

^b Value provided by the supplier.

^c By infrared spectroscopy.

Infrared Spectroscopy. The structural study was 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 moulding to have a mean thickness of 200 μm . The spectra were obtained after 125 scans at a resolution of 2 cm^{-1} .

The assignment of the bands has been undertaken according to Krim²⁴ and Snyder.²⁵ The infrared study has been focused on the polyethylene wagging spectral region. In theory, there may be a great number of conformations which would give rise to infrared bands. However, certain factors reduce this quantity to a few short isomeric sequences of trans and gauche units.²⁶ Due to the high coupling of trans units, the bands appearing between 1300 and 1370 cm^{-1} have their origin from gauche-trans isolated sequences of a few methylene units. In this region there are three characteristic peaks:

1. 1368 cm^{-1} : CH_2 wagging mode in *gtg* and *gtg'* conformations.
2. 1352 cm^{-1} : CH_2 wagging mode in *gg* conformations.
3. 1304 cm^{-1} : CH_2 wagging mode in *gtg* and *gtg'* conformations.

All these bands are very sensitive to conformational changes, as has been pointed out by Painter et al.,²⁶ so that they allow us to detect from their intensities the conformational changes associated to the different crystallization conditions.

For the sake of comparison, the reduced structure factor (RSF) of the bands given above has been calculated. This structural factor can be defined according to the following equation:

$$RSF = A_x/A_{909} \quad (2)$$

where A_x and A_{909} are the absorbances of the bands at $x \text{ cm}^{-1}$ and 909 cm^{-1} (this band being associated with the wagging vibration of end $\text{CH}=\text{CH}_2$ groups²⁷). The RSF is independent of the changes in crystallinity and thickness of the samples.^{28,29}

The methyl group concentration has been calculated by infrared spectroscopy on quenched films using the equation by Bryant and Voter.³⁰ Better resolution of the peak at 1377 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 cm^{-1} .

Dynamic Mechanical Thermal Analysis (DMTA). The mechanical analysis was performed in a Polymer Laboratories DMTA apparatus. The mechanical mode used was the bending one, sharp knifelike supports.²³ 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 mentioned before. 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 parabola method.

The activation energy calculations have been performed using five different frequencies ranging from 0.3 to 30 Hz. The activation energy values were obtained from the slope of the plot of the logarithm of the test frequency as a function of the inverse of the resonance temperature.²

RESULTS AND DISCUSSION

As has been pointed out in the Introduction of this paper, our aim is to deepen in the variables which control the mechanical behavior of high crystalline polyethylene. The most striking feature of this polymer (and of the type of polymers classified by Boyd³ as high crystallinity polymers) is the presence of an α -relaxation which originates in the crystal phase. Hereafter, results relating crystallinity parameters as well as conformational studies will be presented together with a mechanical behavior analysis of the four HDPE samples (Table I). For the sake of clarity, the DTA data will be presented first, followed by the infrared results and, finally, the mechanical studies.

Thermal Analysis. Degree of Segregation and Kinetic Properties

In this first section, the thermal characterization carried out on the four HDPE samples is presented. This thermal study was aimed at determining the relationship between molecular segregation and crystallization temperature, the existence of different crystallization regimes, and the influence of molecular structure on the crystallization kinetics.

Prior to the exposition of the isothermal results, it is interesting to point out that the overall crystallinity changes from 0.77 to 0.87 for sample 8065, from 0.66 to 0.75 for material 2505, from 0.7 to 0.77 for material 4255, and from 0.61 to 0.69 for sample 4005 depending on thermal history.

The relation between the weight fraction of segregated material (calculated from melting data as the ratio between the area of the endotherm due to the segregated material and the total area of the peak²⁰) and crystallization temperature has been plotted in Figure 1 for the four HDPE samples. This figure makes clearer the influence of molecular weight distribution and branch content in the melting behavior of these samples (see Table I). This figure correlates with the molecular characteristics given in Table I, from which it is possible to conclude that:

1. The highly linear material 8065 presents the lowest level of segregated material weight fraction all over the studied temperature range.
2. The molecular weight differences between materials 4255 and 2505 give rise to a distinctly different behavior of the segregated fraction, although both show the same kind of dependence.
3. The highly branched low molecular weight material 4005 displays the highest level of molecular segregation.

These results are in accordance with the conclusions drawn by Gedde and Jansson,²⁰ who pointed out the influence of chain defects on the ability of each molecule to crystallize.

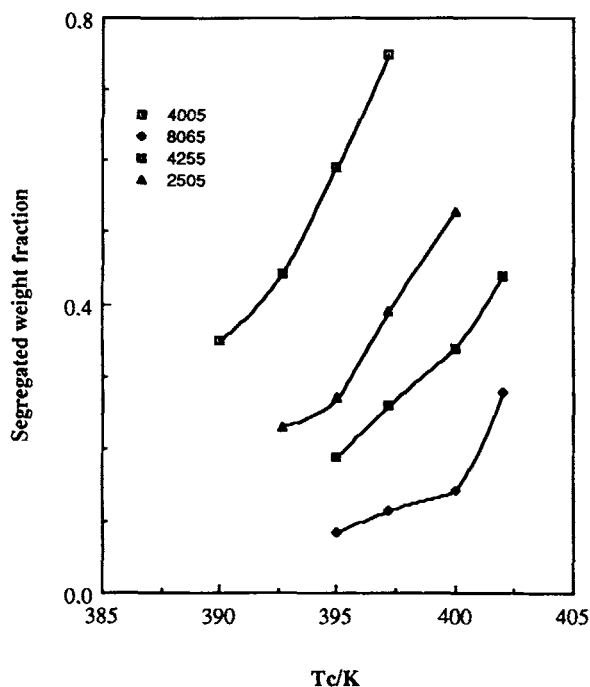


Fig. 1. Segregated material weight fraction as a function of crystallization temperature.

The influence of molecular characteristics on kinetic properties is also of great importance. By plotting the inverse of the decimal logarithm of the semi-crystallization time data ($t_{0.5}$) as a function of crystallization temperature (Fig. 2), this influence becomes apparent. Although the curves are essentially parallel, they shift along the temperature axis depending upon molecular weight distribution and branch content. In Figure 2, the existence of two different types of crystallization regimes³¹ becomes apparent for the four samples. In order to establish the thermodynamic parameters of crystallization inherent to each sample, eq. (1), which is related to the nucleation theory, has been applied.

Whenever a theory of crystallization is to be used, the knowledge of the equilibrium melting temperature (T_M^0) is essential. However, the calculation of this magnitude represents a great drawback for these theories due to the experimental difficulties inherent to its definition. In this work, two different methods have been used to determine T_M^0 : (a) Taking the T_M^0 value for the highly linear sample 8065 equal to 419 K and assuming that the shift along the temperature axis (Fig. 2) corresponds to a shift in T_M^0 . This shift has been calculated at $\log t_{0.5} = 1.5$. (b) Calculating the melting temperature of the equilibrium crystal assuming a Bernoulli distribution for the length of the chain segments between branches [eq. (3)], a crystal thickness controlled by this length, and the applicability of the Thomson-Gibbs equation [eq. (4)]:

$$W(n) = n(1-p)^2 p^{(n-1)} \quad (3)$$

$$T_M^0 = 419.7(1 - 2\sigma_e) / (\Delta h_f \langle n \rangle \langle \cos \phi \rangle l_c) \quad (4)$$

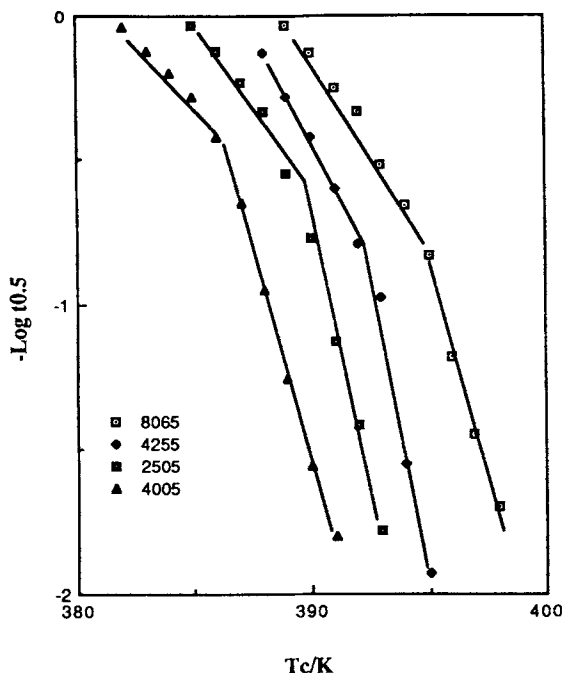


Fig. 2. $-\log t_{0.5}$ plotted as a function of crystallization temperature.

where $W(n)$ is the weight fraction of unbranched segments, n is the number of carbons in the unbranched segments, $(1 - p)$ is the branching probability per main chain, $\langle n \rangle$ is the n mean value accounting for chain branching data (Table I), eq. (3) and DTA results, ϕ is the fold surface free energy (a value of 93 mJ/m^2 ³¹ has been taken in this case), $\langle \cos \phi \rangle$ is the average cosine of the chain tilt angle ($\phi = 30^\circ$ in this analysis), and l_c is the projected carbon-carbon bond length (0.127 nm).³²

Once the equilibrium melting temperature has been determined, the application of eq. (1) is possible. The summary of all the crystallization rate data obtained using this equation is presented in Table II. It is noticeable from this table that:

TABLE II
Crystallization Kinetics of the Four High Density Polyethylene Fractions

Polymer	$T_m^0/\Delta T^a$	$T_m^0/\Delta T^b$	$K_g(\text{I})/K_g(\text{II})^a$	$K_g(\text{I})/K_g(\text{II})^b$
8065	419/24.5	418.6/24.1	160,700/97,840	155,400/94,680
4255	415.9/23.9	415.9/23.9	198,800/111,650	—
2505	411.7/25.3	405.6/19.6	155,000/77,570	81,550/46,290
4005	414.0/25.5	415.6/27.1	159,700/79,830	185,200/89,550

^a Data obtained applying the first method described in the text.

^b Data obtained applying the second method described in the text.

1. All of the samples display two crystallization regimes, which, in accordance with theory,³¹ correspond to two different crystallization modes and morphologies.
2. The values found for the K_g values in both regimes lie below the literature values^{22,23,32} in spite of the equilibrium melting temperature used in this analysis.
3. The supercooling for which the change of crystallization regime takes place is much higher than those reported in the literature.^{22,23,32} The values obtained for this break point are more uniform for the first set of equilibrium melting temperatures than for the second one. This behavior can be explained if the values of branch content determined by infrared spectroscopy are somewhat incorrect (these values were used, as has already been pointed out, for the determination of $\langle n \rangle$).

These discrepancies with respect to studies of almost monodisperse linear polyethylene²² are mainly due to the presence of low molecular weight species which act as diluents and shift the crystallization temperature range towards lower temperatures. Our calculations of the equilibrium melting temperature do not account for this molecular feature and, thus, their values are overestimated. This overestimation emphasizes the low K_g values which are explained by the presence of a more disordered and thicker interlamellar phase than that present in monodisperse linear polyethylene.²²

In the following sections the infrared and thermomechanical data will be presented. These studies have been carried out on samples isothermally crystallized in regime I of crystallization and in quenched samples. The choice of the isothermal crystallization in regime I comes about because of the necessity to prevent nonisothermal crystallization.

Infrared Studies. Reorganization Factor

As mentioned in the Experimental section, the infrared study will be focused on the spectral region corresponding to the wagging vibrations of short segments containing gauche conformations. This region is well known to be very sensitive to thermal history.²⁶ To account for this property, an attempt to relate fold structure and crystallization temperature has been done. Prior to presenting the results, it is convenient to define the reorganization factor R_x as

$$R_x = R_{SF_x} / R_{SF}_{(\text{air-quenched})} \quad (5)$$

This factor enable us to compare the spectra of isothermally crystallized samples with the most disordered sample (the air-quenched one). Thus, its value will vary between 0 and 1, corresponding in the first case to an extended chain equilibrium crystal and in the second one to the quenched sample.

The results obtained from this analysis are summarized in Figures 3–6. All these figures contain information concerning the amorphous region, the assignment of which was established in a previous section. These results must be considered as qualitative indications of the influence of thermal history on the spectroscopic behavior of the HDPE fractions due to the complex character inherent to these vibrations.

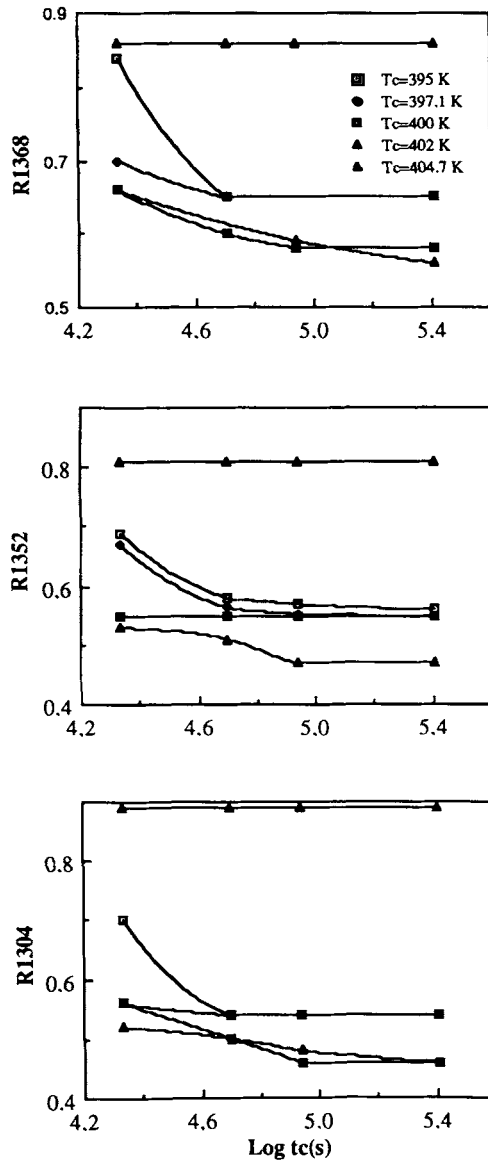


Fig. 3. Reorganization factor plotted vs. the logarithm of crystallization time for material 8065. Each curve corresponds to a different crystallization temperature.

A careful examination of these plots brings about the fact that there are three common features to these samples all:

1. The three wagging vibrations modes behave in a similar way for all of the four samples.
2. The reorganization factor is always smaller than 1 even for those temperatures where no isothermal crystallization takes place.
3. There exists a critical temperature, different for each sample, beyond

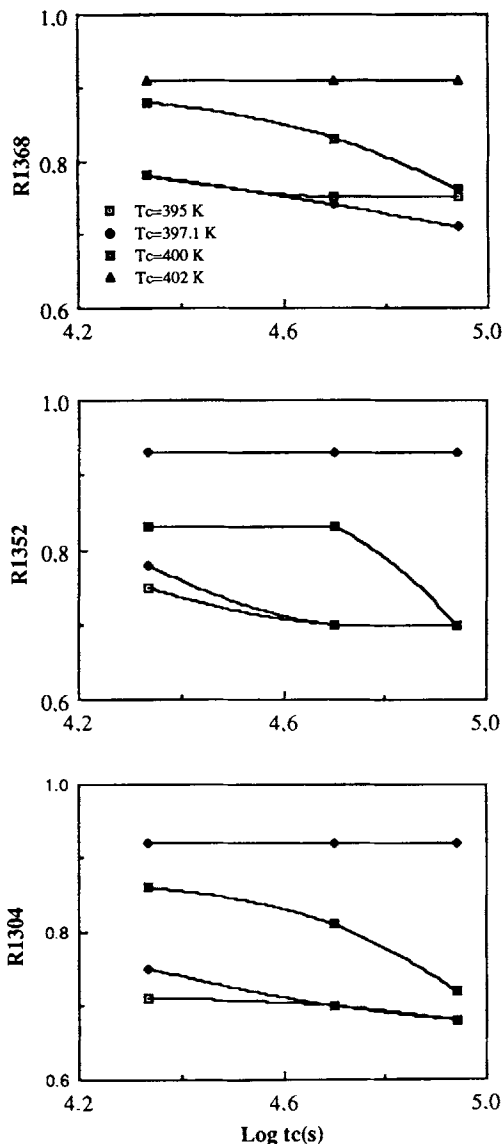


Fig. 4. Reorganization factor plotted vs. the logarithm of crystallization time for material 4255.

which the reorganization factor remains constant and displays the largest values. Together with this critical temperature there is an optimum temperature for which R_x displays the lowest value. This depends on the structural characteristics of each sample.

Molecular segregation plays an important role when the amount of segregated material is high enough as to be detected. This was not the case for fraction 8065 which displays the same spectroscopic behavior over the entire temperature range where isothermal crystallization takes place (up to 402 K). The maximum

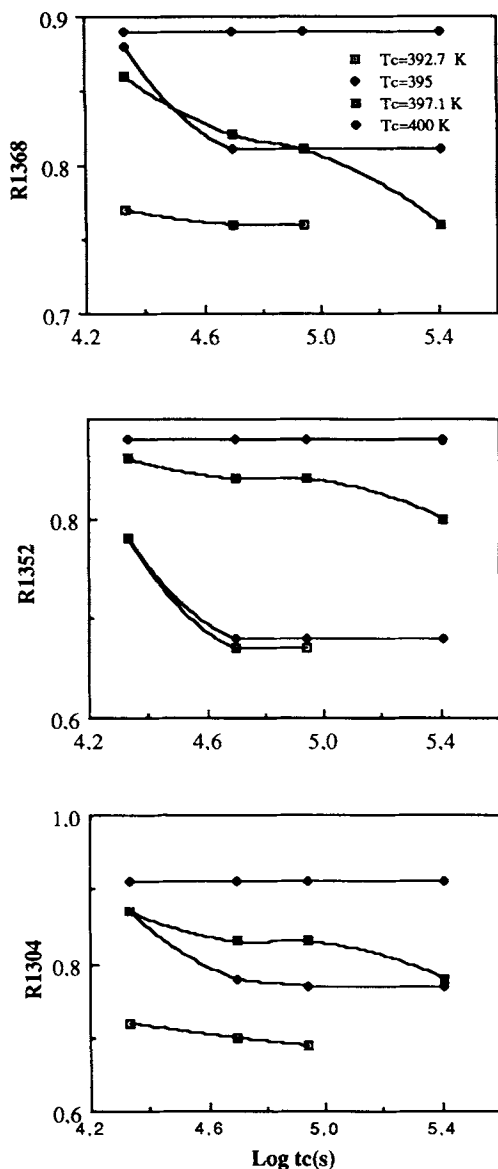


Fig. 5. Reorganization factor plotted vs. the logarithm of crystallization time for material 2505.

of segregated material weight fraction obtained for this material is 0.27 at 402 K. However, there exists a temperature for which the reorganization factor becomes higher due to molecular segregation for the other three fractions. These temperatures are: 402 K for material 4255 (segregated material weight fraction = 0.44); 400 K for material 2505 (segregated material weight fraction = 0.53); and 397 K for material 4005 (segregated material weight fraction = 0.75).

A final important observation to be pointed out is that the reorganization factor decreases as the branch content increases. The optimum R_x value for

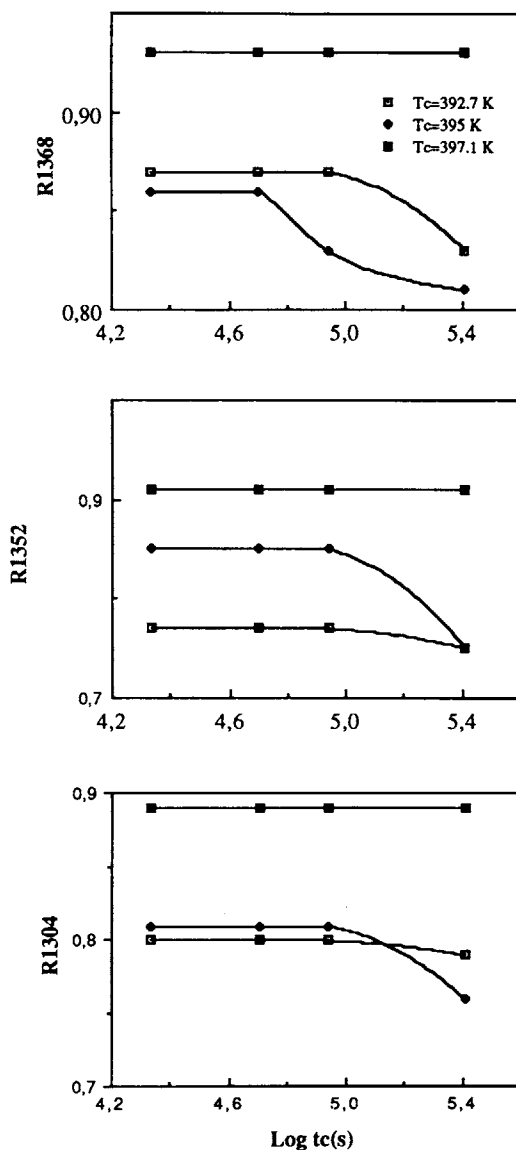


Fig. 6. Reorganization factor plotted vs. the logarithm of crystallization time for material 4005.

the four samples are: 0.5 for material 8065, 0.68 for samples 4255 and 2505, and 0.75 for material 4005. Therefore, the reorganization ability is greater for those materials which show a larger mean length of unbranched segments. This result will be of great importance in explaining the dynamic mechanical results presented in next section.

Dynamic Mechanical Behavior

The previous characterization of the four materials allows us to explain the mechanical behavior of these samples. It is important to keep in mind the role

played by molecular segregation and reorganization ability in the crystalline and amorphous phases.

The analysis of the influence of thermal history on the mechanical spectra of polyethylene shows, in accordance with other literature results,^{3,14} that the transition most dependent on that variable is the α -relaxation. This dependence can be observed in Figures 7–10.

Taking into account that the α -relaxation temperatures corresponding to the air quenched samples are 321 K for material 8065, 314 for material 4255, 312 for material 2505, and 306 for material 4005, the following observations can be drawn from these figures:

1. The transition temperature obtained with isothermally treated samples are always higher than the temperature obtained for the air quenched ones. This is true even for those crystallization temperatures for which no crystallization takes place (very probably due to a slower crystallization rate when the quenching is carried out from this temperature).
2. If ΔT is defined as the difference between the highest transition temperature for isothermally crystallized samples and the transition temperature for the quenched ones, it is observed that material 8065 presents the largest value of this quantity which decreases with increasing branch content (Table III).
3. In all the materials an increase of crystallization time brings about a higher transition temperature.
4. There exists a temperature for which the effect of molecular segregation

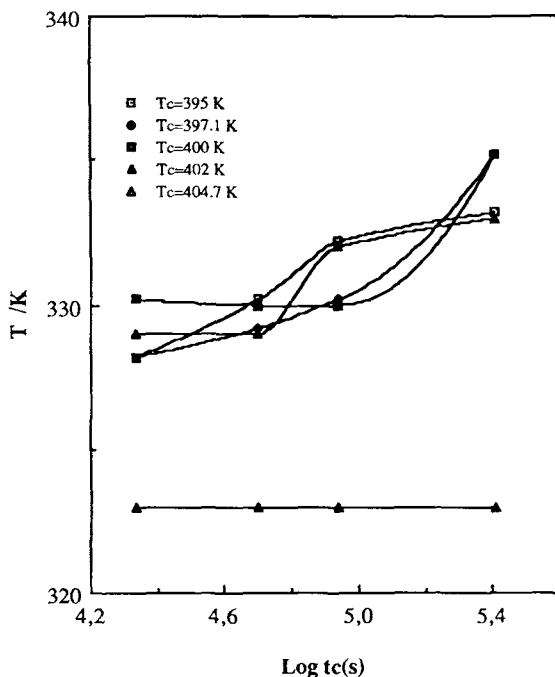


Fig. 7. Change of the α -relaxation as a function of crystallization conditions for material 8065.

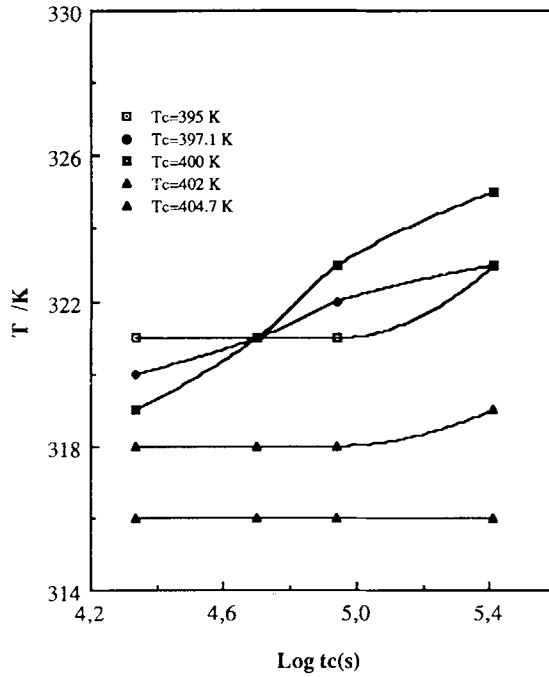


Fig. 8. Change of the α -relaxation as a function of crystallization conditions for material 4255.

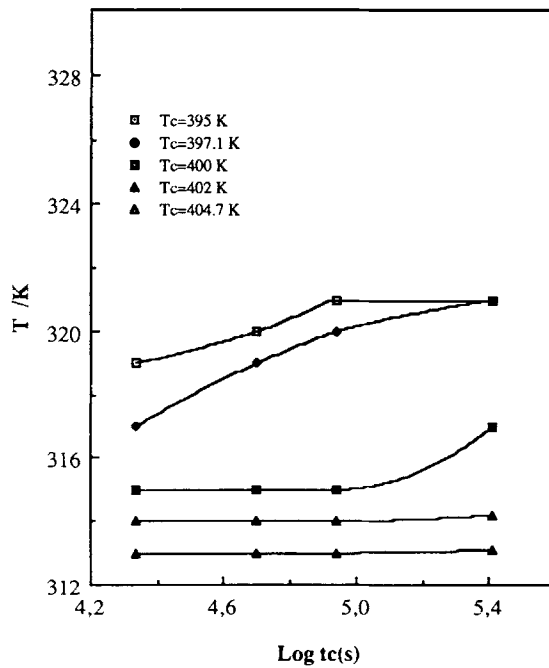


Fig. 9. Change of the α -relaxation as a function of crystallization conditions for material 2505.

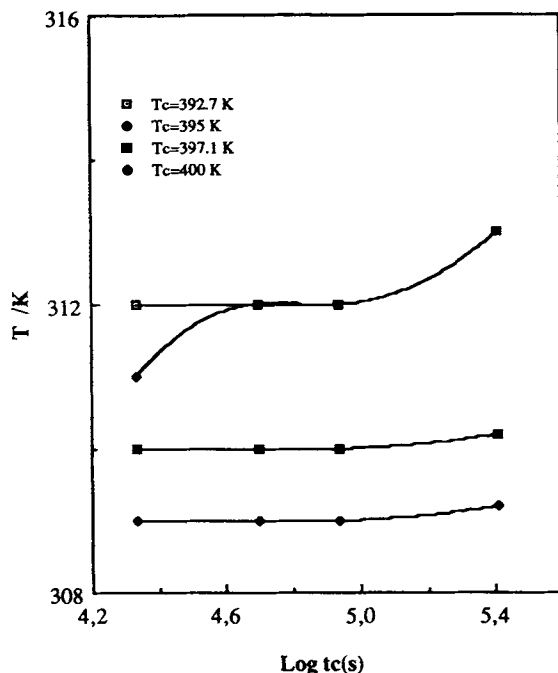


Fig. 10. Change of the α -relaxation as a function of crystallization conditions for material 4005.

becomes apparent. The temperature showing this behavior has already been listed in the infrared spectroscopy section. Molecular segregation produces a decrease in the α -relaxation temperature, even though isothermal thickening has taken place. The asymmetry found for the α -relaxation peak in these cases suggests the presence of a lamellar thickness distribution.

These results can be explained if we refer to the infrared data presented before. In the previous section, it was stated that the reorganization factor showed a value always smaller than one, this being an indication of the formation of a different lamellar thickness distribution with respect to the air-quenched sam-

TABLE III
Some Aspects of the Relaxation Data of the HDPE Fractions

Polymer	T (air-quenched)	ΔT	E_a (air-quenched) (kJ/mol)	$E_a (I)$ (kJ/mol) ^a
8065	321	14	124	180
4255	314	11	123	200
2505	312	9	127	167
4005	306	7	134	175

^a Activation energy data obtained from samples isothermally thickened in regime I of crystallization.

ples, depending on thermal history. A careful examination of the corresponding infrared and mechanical spectra data for each sample shows that both techniques give rise to similar results. In fact, the relaxation temperatures found for the isothermally treated samples, always larger than the value of the corresponding air-quenched one, agrees with the infrared results. The infrared data showed that the largest reorganization capacity corresponded to the almost linear material 8065 and that this capacity must, therefore, be connected to the change in the position of the α transition, which presents the highest value for the most linear material and decreases with the branch content. This shift of the transition along the the temperature axis suggests a change in the activation energy as the fold period increases as a consequence of isothermal thickening.

In order to corroborate this hypothesis, activation energy calculations were carried out as a function of thermal history assuming an Arrhenius type dependence for the dynamic mechanical data of our materials.² Figure 11 is an example of the type of experimental curves obtained when the frequency of the test is changed. Higher frequencies imply higher resonance temperature. By plotting the logarithm of the frequency as a function of the inverse of the resonance temperature, the activation energy can be readily obtained from the slope. The results obtained from these calculations are summed up in Table III. These results indicate that the activation energy is smaller in the air-quenched samples than in the isothermally thickened ones. Thus, the increase in fold period gives rise to a new distribution of segments within the amorphous layer, decreasing the number of folds, this being the reason for the change in

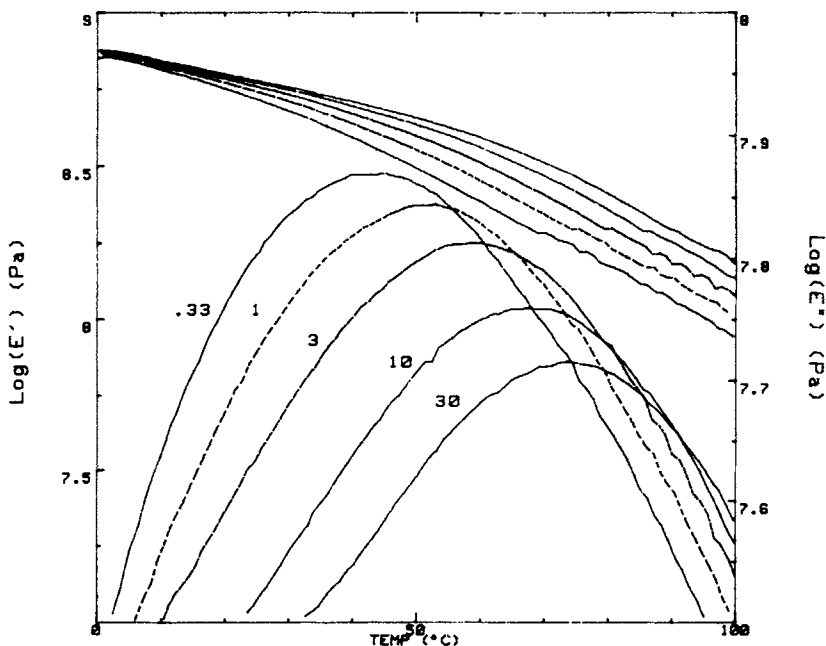


Fig. 11. Variation of the loss and storage modulus as a function of temperature and frequency. The slope of the plot log frequency vs. the inverse of the absolute temperature is the activation energy of the process.²

the resonance conditions for the transition. The values reported in Table III must be considered only as qualitative indications of the trend of the set of materials investigated due to the difficulties inherent to the experimental determination of this parameter (sample imperfections and broad relaxations).

The increase in the α transition temperature as a function of crystallization time can be explained on the basis of the data by Gedde and Jansson.²⁰ According to these authors, the melting temperature changes linearly with crystallization time. In our study, all the measurements have been done in what they called stage 2 of crystallization.²⁰ This increment of the high temperature melting peak is related to the isothermally formed crystal thickness through the Thomson-Gibbs equation.³² Therefore, the increase in the α -relaxation temperature is related to the mean lamellar thickness. The infrared data show that, similarly to the dynamic mechanical results, the reorganization factor decreases with increasing crystallization time as a consequence of a decrease of the amorphous interlamellar layer.

An important consequence of this study arises from the fact that all the dynamic mechanical measurements as well as the infrared determinations have been carried out in regime I of crystallization where the polyethylene crystals displays an axialite type morphology for the molecular weights we are using in this study.³¹ Therefore, the supermolecular structure does not play a vital role in the mechanical behavior of this materials.

Finally, no secondary crystalline relaxation transitions^{14,15} have been observed in this study, even though all the mechanical curves were analyzed using derivative methods; the loss modulus was represented as a function of $1/T$, which is said to be a good method for separating the contributions of the ab-

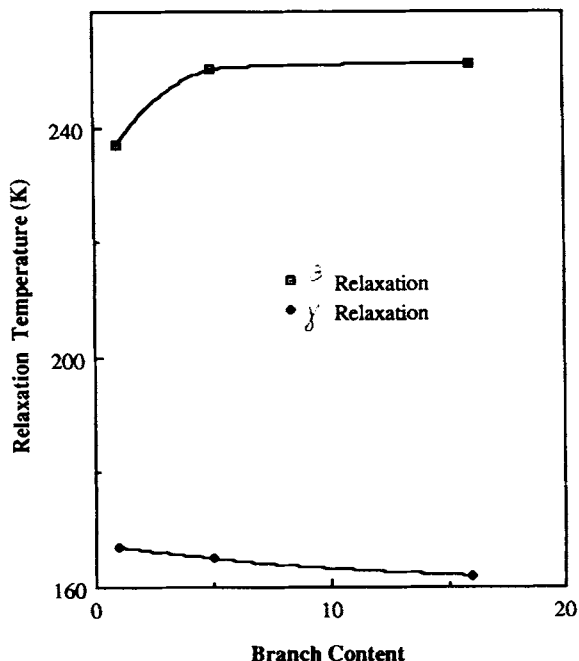


Fig. 12. Change of the mean β - and γ -relaxation temperatures as a function of branch content.

sorption due to perfect crystalline regions (herein associated with the isothermally grown crystals) and the absorption due to the defective crystalline region (herein associated to the segregated material). Only when the amount of segregated material becomes important, some asymmetry, as has been pointed out above, was detected in the relaxation peak. Again, the infrared spectroscopy and mechanical data are in agreement and provide evidence for the influence of molecular segregation on the dynamic mechanical properties. Further work involving the analysis of blends of different polyethylenes (high density, low density, and linear low density polyethylenes) is being carried out in our laboratories in order to clarify this point.

As mentioned above, the β - and γ -relaxations do not present a measurable dependence on thermal history within the same sample. However, their mean values vary depending on branch content. Figure 12 shows this change, while Figure 13 the change of the mean relaxation strength for the three transitions as a function of branch content. It is outstanding from these figures that:

1. The β -relaxation temperature is lower for material 8065 than for the more highly branched ones.
2. The γ -relaxation remains fairly constant throughout the whole branch content range.
3. The mean relaxation strengths associated with the β - and γ -relaxations do not depend on the branch content, while the mean relaxation strength of the α -relaxation is a function of branch content.

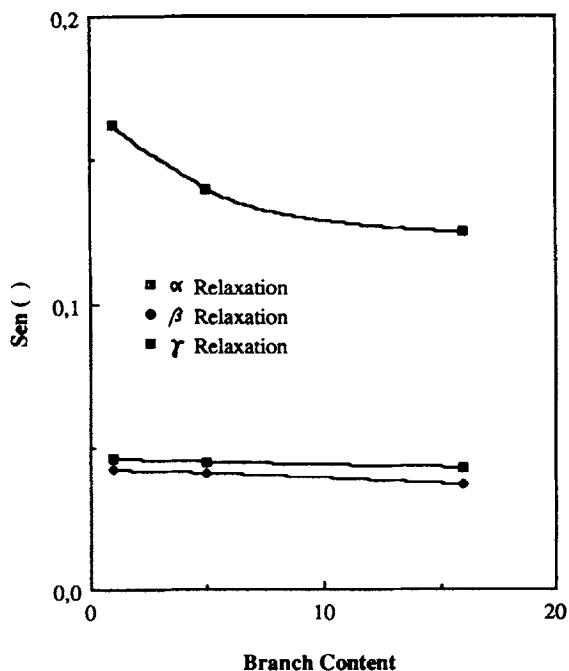


Fig. 13. Variation of the mean α -, β -, and γ -relaxation strengths as a function of branch content.

The first observation represents a striking behavior which must be explained by accounting for the nature of the amorphous phase in the interlamellar layer. The two last observations agree with the data by Boyd.¹⁶

CONCLUSIONS

Crystallization kinetics and structural and dynamic mechanical studies of four HDPE samples allow us to draw the following conclusions: (1) The α -relaxation is the transition which experiences a major change as a function of supercooling; (2) the reorganization factor is a function of the crystallization conditions as well as of the mean length of chain segments between branches; (3) molecular segregation plays an important role in the dynamic mechanical behavior; (4) morphology does not influence the mechanical spectra of the samples; (5) the resonance temperature for the β -relaxation depends mainly on the branch content of the fractions; and (6) the α -relaxation strength is affected by branch content, while both the β - and γ -relaxations strengths keep constant regardless of this branch content for the four HDPE studied.

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