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Cooperativity in the Crystalline α-Relaxation of Polyethylene

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Introduction. Even though the origin and mechanisms of the α-process in polyethylene (PE) have been extensively investigated,[1−3] one question that is not fully understood is the cooperative nature of this process. Is the α-process simple, involving only motion of chains that do not interfere with the neighboring groups of atoms or molecules, or, on the contrary, do the molecular motions assigned to this process involve, in part, a range of related motions within an appreciable correlation volume? Starkweather formalism was shown to be a suitable tool for assigning a relaxation as either "complex" (cooperative in nature) or "simple" (localized mobility).[4,5] This procedure is based on the use of the concept of activation entropy, where the activation energy of the process is compared to the activation energy of a zero-entropy (noncooperative) process. In this work, dielectric spectroscopy, NMR, and mechanical spectroscopy results will be analyzed in order to understand the extent of the cooperative character of the α-relaxation in PE.

As referred by Hu et al., important properties are influenced by this relaxation such as creep, annealing, crystallization, extrudability, and drawability.[6] Moreover, it has been shown that the α-process of PE is very similar in nature to the same process observed in a variety of flexible semicrystalline polymers, including poly(methylene oxide), poly(ethylene oxide), or isotactic polypropylene.[2,3] These are the arguments for continuing the investigation until the complete elucidation of the mechanisms associated with this process.

Experimental Section. The material studied by mechanical relaxation spectroscopy was a high-density polyethylene, HDPE (grade HD8621, from DSM, The Netherlands), with a number-average molecular weight ($\langle M_n \rangle$) of 7.0×10^3 and a weight-average molecular weight ($\langle M_w \rangle$) of 2.1×10^5. The samples were prepared by injection molding. Two different processing modes were used: conventional injection molding (CIM) and shear-controlled orientation in injection molding (SCORIM). The later technology relies on the application of shear stress fields to the melt/solid interfaces during the packing stage by means of hydraulically actuated pistons.[7] After the filling of the cavity mold, the molten polymer is continuously sheared as the solidification progressively occurs from the mold wall to the molding core part. As a result of SCORIM processing, a highly sheared crystalline phase of PE can be obtained, exhibiting a significant improvement of anisotropy.[8,9] In the text the HDPE samples processed by CIM and SCORIM will be named isotropic PE and anisotropic PE, respectively. More details concerning the processing of the material and the mechanical performances of the molds can be found in ref 9. The dynamic mechanical properties of the samples (axysymmetric tensile test bars with 5 mm diameter) were studied with a Perkin-Elmer DMA7e under flexural mode using 1.2×10^5 and 1.0×10^5 Pa static and dynamic stresses, respectively. Frequency scans, from 0.5 to 30 Hz, were carried out at different temperatures, from 0 to 95 °C.

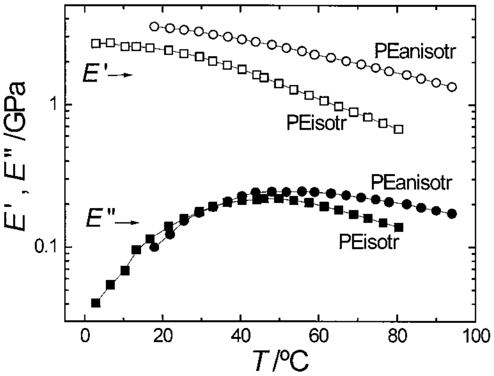

Figure 1. Storage modulus (open symbols) and loss modulus (filled symbols) for a high-density PE in the α-relaxation region for a frequency of 1 Hz. Square: isotropic PE obtained by conventional injection molding. Circles: anisotropic PE processed by SCORIM.

The NMR and dielectric results were taken from the literature.[10,11]

Results and Discussion. Dielectric and mechanical spectroscopies have been often used for studying the α-relaxation.[1−3,12,13] The α-process is dielectrically active due to the reorientation of carbonyl group defects in the chains in the crystalline phase.[1−3] However, those screw motions occur between energetically equivalent states and, thus, could not contribute for the mechanical relaxation. The mechanical α-relaxation emerges from an additional shear of the amorphous regions that occur naturally during the chain transport through the lamellae, enabling energy dissipation.[1−3] The participation of the amorphous phase in the mechanical α-relaxation is consistent with the broad distribution of characteristic times observed for this case, in contrast with a quasi-Debye behavior for the dielectric α-relaxation. Some authors claim a very complex nature for the mechanical α-relaxation, consisting of two independent relaxation processes (αI and αII processes)[14,15] or even three,[16,17] with activation energies ranging from 90 to more than 300 kJ mol^{-1}.[1−3] It seems unequivocal that the crystalline phase plays a fundamental role for the appearance of the α-relaxation, namely through 180° flip motions of the chain stems in the crystalline lamellae.[1−3] This screw motion process, involving both rotational and translational mobility within the chains, was detected by ^{13}C NMR.[6]

The temperature dependence of the storage and loss moduli for the frequency of 1 Hz, taken for the isothermal data in the α-relaxation region on the isotropic and anisotropic PE, is plotted in Figure 1. As found in the $E''(T)$ plot in Figure 1, other works reported a broad mechanical α-peak in the loss modulus spectrum along the temperature and frequency axis (for example, refs 12 and 16). This fact is related to the broad distribution of characteristic times associated with this process. For example, the Cole−Cole α-parameter, which is related to the breadth of this distribution, was found to be higher than 0.75 in the same system studied in this

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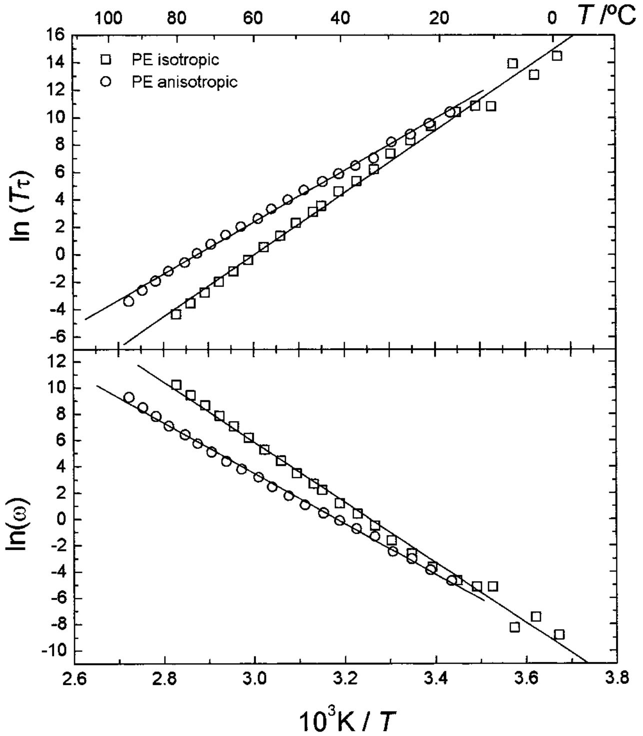

Figure 2. Eyring (top graphics) and Arrhenius (bottom graphics) plots for the α-relaxation of materials in Figure 1 obtained from mechanical spectroscopy (same symbols). The solid lines are the linear fits of the experimental data.

work.[9] Obviously, the position of the loss modulus peak depends on the frequency. Many authors used the Arrhenius equation to correlate frequency and the temperature of maximum E'' for the α-relaxation of PE:

$$f = f_0 \exp[-E_a/RT] \tag{1}$$

where f is the frequency, related to the angular frequency, ω, by $\omega = 2\pi f$, f_0 is a preexponential factor, E_a is the activation energy, and R is the perfect gas constant. A similar relationship is derived from Eyring's theory of absolute reaction rates:

$$f = \frac{kT}{2\pi h} \exp(\Delta S/R) \exp(-\Delta H/RT) \tag{2}$$

where ΔS and ΔH are the activation entropy and enthalpy, respectively and k and h are respectively the Boltzmann and Planck constants. The use of eqs 1 and 2 presupposes a thermally activated behavior of the studied process, which we will assume for the case of the α-relaxation of polyethylene, although there might be some arguments against it.[9]

The thermokinetic parameters may be easily obtained from the experimental data using eqs 1 and 2. The Arrhenius and Eyring plots for the studied polyethylenes are shown in Figure 2. Those plots were obtained from the temperature shift factors that were necessary to construct the master curve from the isothermal results and from the knowledge of a $\tau(T)$ point for each material, which was obtained by looking at the temperatures of maximum E'' at 1 Hz.

The Arrhenius plot of the two materials suggests that as the temperature increases, the characteristic times of the oriented material are getting smaller, relative to the more isotropic sample. For example, at 80 °C the relaxation times of the isotropic and an isotropic materials are 1.1×10^{-3} and 6.1×10^{-5} s, respectively, that is, ca. 18 times higher for the former. This observation has been used to associate the effect that the α-relaxation has on the gradual strain hardening of PE during high-temperature draw.[6] In fact, Hu et al. related the solid-state drawability of PE to the chain translation in the crystalline phase associated with the α-relaxation.[6]

The fits in Figure 2 yield, for the isotropic PE, $\Delta H = 188$ kJ mol^{-1}, $\Delta S = 367$ J K^{-1} mol^{-1}, and $E_a = 190$ kJ mol^{-1} and, for the anisotropic PE, $\Delta H = 157$ kJ mol^{-1}, $\Delta S = 255$ J K^{-1} mol^{-1}, and $E_a = 160$ kJ mol^{-1}.

Values of activation energies of the α-relaxation of PE are often reported in kinetic studies. Usually such values are discussed in terms of energy barriers needed to be surpassed by the relaxing entities and their correlation with the structure or morphology of the studied materials. In this work the obtained activation energies will be combined with the temperature position of the process, at a given frequency, to obtain further information concerning the cooperative character of the α-relaxation of PE. Note that the reported E_a values are obtained from the fit of the data in the entire studied temperature range. It was previously suggested that the results could include the presence of both αI and αII processes,[9] which contain contributions of intralamellar and intracrystalline relaxations, respectively.[12] The former process appears in the low-temperature region and yields activation energies of 175 and 151 kJ mol^{-1} for the isotropic and anisotropic samples, respectively. On the other hand, the αII process appears at higher temperatures where the activation energies are 208 and 182 kJ mol^{-1} for the same two materials. The obtained activation energies are higher than the ones reported in the literature for dielectric results, which are close to 110 kJ mol^{-1}.[1-3,9] However, activation energies obtained from mechanical measurements of the order of the ones obtained in the studied samples are also reported (e.g., refs 12 and 18). The origin of such strong variation of the activation energies observed in the mechanical α-relaxation of PE was not yet clearly elucidated. Probably, the lamellar thickness and the general morphology at the nanometer scale will have an influence.

The activation energy and enthalpy of eqs 1 and 2 are related by[19]

$$E_a = \Delta H + RT - P\Delta V \tag{3}$$

where ΔV is the activation volume and P is the pressure. Neglecting the $P\Delta V$ term, due to its low magnitude, we may write, from eqs 1−3,

$$E_a = RT[1 + \ln(kT/2\pi hf)] + T\Delta S \tag{4}$$

For a given temperature and frequency, it was suggested that the lower limit of the activation energy of viscoelastic relaxations is found for zero activation entropy.[4] In that case eq 4 reduces, with $\Delta S = 0$, to

$$E_a = RT[22.92 + \ln(T/f)] \tag{5}$$

This lower limit should reflect processes characterized by local and noncooperative motions ("simple relaxations").[4,5,20] In such processes the interactions between the relaxing entities and the neighboring atoms or molecules are of short range. On the other hand, activation energies well above this zero-entropy condi-

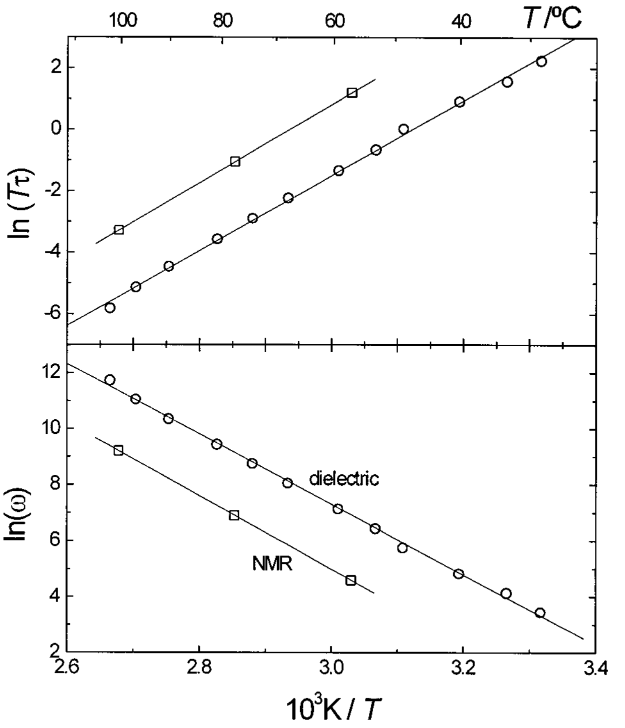

Figure 3. Eyring (top graphics) and Arrhenius (bottom graphics) plots for polyethylenes studied by dielectric spectroscopy (circles) and NMR (squares). The solid lines are the linear fits of the experimental data.

tions are ascribed to processes with a cooperative character (“complex relaxations”). Many low-temperature relaxations, such as some β-relaxations in amorphous materials, discussed by Starkweather showed more or less a deviation from the zero entropy line in a E_a vs T plot, for a given frequency (usually $f = 1$ Hz). However, a very local process was found in PE below 5 K with very small absolute values of activation entropy, ascribed to a quantum mechanical tunneling process.[21] Other “simple” δ- or γ-relaxations also presented small activation entropies.[4] Such studies demonstrate that local processes have negligible activation energies. This simple zero-entropy criterion may be very useful for characterizing the cooperative character of relaxation processes and was shown to be applicable also in low-molecular-weight systems.[22] It must be remarked that this “zero-entropy” criterion must be regarded as a comparative method that allows to distinguish the cooperativity extent of different relaxations. This may be informative about the mechanisms associated with a given relaxation, such as the crystalline α-relaxation of polyethylene analyzed in this work. However, in a first analysis, no quantitative information (for example, the estimation of the correlation lengths of the motions) may be directly extracted with this method.

Beside the viscoelastic data, presented in this work, it would also be interesting to include results of the α-relaxation of PE obtained with other techniques in order to follow the just mentioned comparative strategy. Figure 3 shows the Arrhenius and Eyring plots relative to data collected elsewhere from dielectric spectroscopy[10] and NMR[11] studies on PE. The fits yield, for the dielectric data, $\Delta H = 102$ kJ mol^{-1}, $\Delta S = 120$ J K^{-1} mol^{-1}, and $E_a = 104$ kJ mol^{-1} and, for the NMR results, $\Delta H = 106$ kJ mol^{-1}, $\Delta S = 113$ J K^{-1} mol^{-1}, and $E_a = 109$ kJ mol^{-1}.

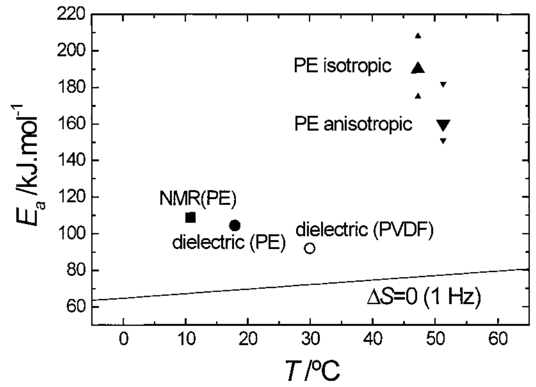

Figure 4. Cooperative plot for the α-relaxation of polyethylene (filled symbols) and of poly(vinylidene fluoride)−PVDF (open circle). Solid line: zero-entropy prediction at $f = 1$ Hz. Filled symbols: activation energies of the α-relaxation of polyethylenes and corresponding position for a frequency of 1 Hz obtained with different techniques. Filled square: NMR result. Filled circle: dielectric relaxation spectroscopy result. The up and down filled triangles are for the mechanical spectroscopy results on the isotropic and anisotropic HDPE reported in this work, respectively. The larger triangles correspond to the overall α-relaxation, and the smaller triangles represent the activation energies obtained in the low-temperature region of the process (low E_a values) and in the high-temperature region of the process (higher values of E_a). Open circle: dielectric relaxation spectroscopy results of the α-relaxation in PVDF between 10^{-1} and 10^5 Hz.[25]

Figure 4 shows a cooperativity plot of apparent activation energy against relaxation temperature (1 Hz) for the dielectric spectroscopy, NMR, and mechanical spectroscopy of the α-relaxation of PE. The limiting case of the activation energy for zero activation energy ($\Delta S = 0$) at 1 Hz is represented by the solid line.

For the mechanical results shown in Figure 4, besides the results of the overall α-process (larger triangles), the results obtained by linear fitting the Arrhenius lines in the low- and high-temperature ranges of the relaxation (smaller triangles) were also included. This corresponds to an attempt to study the cooperativity of the αI (lower E_a values) and the αII processes (higher E_a values). Besides the activation energies, the Arrhenius lines obtained by fitting the data in the low- and high-temperature regions of the α-process also allowed to calculate the temperature position of the αI and αII processes. It was found that, for each material, the temperatures of the two α-processes at 1 Hz are very similar. This similarity may be the reason that the two processes were not discriminated in the mechanical spectrum at 1 Hz (Figure 1). Other studies also reported a single peak in the α-relaxation region for different polyethylenes (see, for example, refs 13, 16, and 18).

In Figure 4, both the dielectric and NMR activation energies deviate, at a similar vertical distance, from the $\Delta S = 0$ case. Note that the vertical distance between the data points and the $\Delta S = 0$ solid line reflects the value of $T\Delta S$. These results suggest some cooperativity in the motions associated with the α-relaxation as studied by these two techniques. In fact, this deviation is found to be higher than the one observed in several secondary relaxations, with assigned cooperative character, reported elsewhere.[4,5,23]

Twist propagation of the CH_2 groups across the crystal has been modeled in atomistic detail, using extensive conformational energy calculations.[24] The most efficient twist contains a series of about 12 CH_2 groups. The activation energy associated with the α-relaxation is related with the energy barriers necessary to create a twist. This twist, once formed, can move through the surrounding lattice with little or no hindrance. Therefore, one should expect that the α-relaxation in PE, as seen by techniques were the chains in the crystalline fraction are directly probed (such as in dielectric spectroscopy and NMR), would have a weak cooperative character. However, Schimdt-Rohr and Spiess demonstrated by 2D exchange ^{13}C NMR that, in the α-relaxation of PE, the chain jump process results in large-scale chain diffusion that is significantly hindered by constraints in the amorphous regions.[11] The release of such constraints during the α-process influences in some extent the kinetics of the motions in the lamellae and, thus, may be the origin of the certain cooperative character of the α-relaxation as seen by NMR and dielectric spectroscopy.

The dielectric α-relaxation of poly(vinylidene fluoride) is also represented in the cooperative plot (open circle in Figure 4), with data extracted from ref 25. The deviation of this point from the zero-entropy line is similar to the dielectric result on PE. Thus, the cooperative character of the crystalline α-relaxation seems to be a general feature of the process, observed not only in PE.

The mechanical spectroscopy results in Figure 4 show a greater deviation from the zero-entropy line than the data from the two other techniques. However, one must be cautious in such analysis: as said before, the mechanical α-relaxation results reported in the literature present a large range of possible activation energies.

In the case of considering the occurrence of the αI and αII processes in the data of this work (lower and high values of E_a shown by the small triangles in Figure 4), one can conclude that these two processes also deviate largely from the zero-entropy prediction. This should be expected due to the fact that the mechanical α-relaxation is directly manifested by the molecular mobility within the amorphous phase. Such motions are often associated with cooperative processes. The best example of cooperativity due to long-range collective mobility in the amorphous phase is the glass transition. The activation energies associated with that process clearly diverges from the zero-entropy prediction (see for example refs 26−28).

Figure 4 shows that the anisotropic material presents a lower cooperative character, when compared with the isotropic one. This behavior suggests a decrease of complexity (number of conformational arrangements) of the activated state of the motions associated with the α-relaxation in a higher oriented medium. The complexity could be quantified in terms of the number of microstates, defined by the possible conformational rearrangements of the activated state that lead to the same prescribed macroscopic properties; i.e., this number would define the Ω parameter of the celebrated Boltzmann's formula $S = k \ln \Omega$. However, this explanation is speculative, and more work would be needed in order to fully understand the difference in cooperativity in the two materials. In a more practical point of view the change of cooperativity results in the difference of activation energies between the two materials. The lower activation enthalpy or energy detected in the anisotropic sample may be a result of less hindered development of molecular motions associated with the α-relaxation due to an higher crystalline order[9] or simply due to differences in the lamellar thickness. This fact is in agreement with the work of Matsuo et al. where linear PE films with increasing orientation showed a continuous decrease of activation energy.[16] If the position of the relaxation in the temperature axis does not change significantly, this decrease of activation energy implies a decrease of ΔS and, therefore, a decrease of cooperativity.

The location of the α-relaxation depends also on the crystalline lamellar thickness.[2] As the position of the process along the frequency axis may be given by eq 2, this effect may have an enthalpic or entropic origin. It would be interesting to represent the data of PE materials with different lamellar thickness in an Eyring plot to elucidate this question. To our knowledge such analysis was never carried out. Such studies could also provide information about the effect of the lamellar thickness on the degree of cooperativity of the α-relaxation.

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