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α, β and γ relaxations of functionalized HD polyethylene: a TSDC and a mechanical study

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Abstract

The relaxation behavior of high density polyethylene functionalized with diethylmaleate has been determined by dynamic mechanical method and thermally stimulated depolarization technique. The transitions observed have been related to the structural parameters as well as the α-olefin comonomer content and degree of grafting, and compared with previous TSDC results on LLPE functionalized with the same polar group. The lowest relaxation is composed of a sub-γ and a γ mode assigned to localized motions of the polar groups and to the glass transition (at 137 K), respectively. The β-relaxation intensity grows with the grafting degree in agreement with its assignment to motions taking place in the interfacial regions. The behavior of the α-mode with different content of diethylmaleate has confirmed its dependence with the crystallite size. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyethylene; Relaxations; Functionalization

1. Introduction

There has been a great interest in recent years in the functionalization of polyolefins in order to modify the non-polar character of these materials [1–5]. Unmodified polyolefins are inmiscible with almost any other polymer. However, the introduction of polar groups capable of showing specific interactions between components can improve the compatibilization of polyolefin blends.

Modification with functional monomers as maleic anhidride and alkyl maleates, has been undertaken with several kinds of polyolefins (high, low and linear low density polyethylenes, polypropylene, ethylene–propylene rubber) [6–10]. The reactions have been carried out under heterogeneous [6–10] and homogeneous [3,4] conditions.

In contrast, the introduction into polyethylene of units that differ chemically from the predominant olefinic chain through the functionalization with polar monomers, will impose restrictions on the mobility of the chains, affecting considerably the solid state properties of these polymers. The study of the differences observed depending on concentration and sequence distribution of the different chain units, will help to understand the modifications produced in the molecular architecture of the chains. Moreover, the presence of polar groups will allow use of dielectric spectroscopy in combination with mechanical techniques to measure the different relaxation modes as a function of temperature, and this will lead to a better understanding of some of the still open questions about the complex relaxation behavior of these materials.

A great deal of work has been reported about the dynamic mechanical [11–17] and dielectric [18–22] behavior of polyethylenes and the influence of the structure and morphology on their relaxations. Polyethylene is not naturally dielectrically active but the functionalization with alkyl maleates modifies its non-polar character. In previous studies, polyethylene has been oxidized or chlorinated [18–20] in order to provide a sufficient number of dipoles to serve as probes in the dielectric experiments. However, very few works are related with the relaxations observed in functionalized polyethylenes. To the best of our knowledge, only a study [23] on maleated high density polyethylene by dynamic mechanical analysis and very recently, a thermally stimulated depolarization currents study [22] on linear low density polyethylene grafted with diethylmaleate, have been carried out in functionalized polyethylenes.

In order of decreasing temperature, linear and branched polyethylenes, as well as copolymers of ethylene, display a series of transitions below the melting temperature that have been conventionally designated as α, β and γ-relaxations [24]. The γ-transition is usually observed in the range

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Table 1
Molecular weight and structure of the original HDPE samples

Sample	Mol.%	Comonomer Wt.%	Type	M_w	M_n	M_w/M_n	ρ (g/cm^3)
HDPE-1	0.8	2.36	Cohexene	175000	18700	9	0.9465
HDPE-2	0.66	1.32	Cobutene	313000	17000	18	0.9493

123–153 K, the β-transition in the range 243–283 K, and the α-transition between 303 and 393 K.

It is generally accepted that the α-transition is associated to motions of chain units which lie within the crystalline region of the polymer. However, several molecular mechanisms have been proposed to interpret this relaxation, such as rotation of the crystalline sequences followed by translation along the chain axis, or torsional twisting in the crystalline sequence among others [21,24]. It has been reported [11,25], that the incorporation of structural and chemical factors into the chain, such as chlorination, branching, or copolymerization with non-crystallizable units, decreased the intensity of this transition and, in some cases, with high chlorine or counit concentration, the relaxation even disappeared [14]. However, it has been demonstrated [12] that the temperature of the transition increases with the crystallite thickness for a series of linear and branched polyethylenes, as well as ethylene–vinyl acetate copolymers and hydrogenated polybutadienes. Thus, the location of the α-transition depends primarily on the crystallite thickness. The level of crystallinity and the supermolecular structure do not seem to play a significant role on the location of the transition.

The origin of the mechanisms involved in the β-transition is still controversial. The transition appears in some polyethylenes as a weak shoulder [26] but in other samples a well defined maximum is observed [11–13]. This transition has been often attributed to a broad glass transition [27]. However, from dynamic mechanical analysis (DMA) studies and analysis of the influence of different structural factors on the transition, Mandelkern et al. [12] concluded that it results from the motion of chain units that are located in the interfacial region.

The γ-relaxation, which has been observed [28,29] in polyethylenes around 153 K, is a complex transition and its origin has been widely discussed. It has been observed that its intensity increases when the crystallinity decreases; therefore, it has been associated to the amorphous region of the semicrystalline polymers and frequently, to the glass transition, T_g [28,29]. However, due to its low activation energy other authors have associated the γ-relaxation with a crankshaft motion of short polymer segments requiring a minimum of three methylene units [30]. In a recent work, Lee et al. [31] reported a thorough study on the mechanical relaxations in LLD, LD and HDPE blends. Their results indicate miscibility in the amorphous phase, with a $T_\gamma = T_g$ shifting linearly between those of each component. This is another important experimental result in favor of the assignment of the γ-mode to the glass transition of the material.

The main objective of this work is to extend previous studies [22] by TSDC on functionalized linear low density polyethylene (LLDPE) to high density polyethylenes (HDPE). Additionally, we have analyzed the relaxations measured by dynamic mechanical (DMA) and thermally stimulated depolarization (TSDC) techniques as a function of the degree of grafting, the α-olefin comonomer content and the structural parameters such as crystallinity, interfacial phase and lamellar thickness. The α, β and γ-relaxations and the type of motions involved in each of them, have been interpreted in high density polyethylene functionalized with diethylmaleate, and compared to those reported on linear low density polyethylene modified with the same polar monomer. The origin of these relaxations has been clarified and some interesting new features have been observed.

2. Experimental

2.1. Materials and sample preparation

The samples used in this study were commercial high density polyethylenes, HDPE, obtained from different manufacturers (Repsol and Hoechst Ibérica S.A.) and the same polymers with different degrees of functionalization with diethylmaleate, DEM. HDPE samples were characterized previously to the modification, following conventional procedures in polymers. Molecular weight characteristics of the original polyethylenes are given in Table 1. Weight and number-average molecular weights were determined by gel permeation chromatography, GPC Densities of the samples were determined at 296 K in a Davenport density gradient column, consisting of a water–ethyl alcohol mixture, calibrated with standard glass floats (see Table 1).

The determination of the counit content in the original samples was carried out by ^{13}C NMR using the corresponding assignments given by Randall [32]. ^{13}C NMR spectra were performed at 75.47 MHz on a Bruker AC-300 spectrometer at 373 K in 1,2,4-trichlorobenzene containing 15% hexadeuterobenzene. Around 10 000 scans with a pulse angle of 45° and a delay of 5 s, 32 Kb memory, and an acquisition time of 1 s were used. The type and concentration of α-olefin are summarized in Table 1.

Table 2
Degree of functionalization and thermal properties determined in dynamic conditions for modified HDPE

Sample	DEM		$(T_m)_{app}$ [a] (K)	T_C [b] (K)	ΔH_a [c] (J/g)	$(1 - \lambda)_{\Delta H_u}$ [d]
	Mol.%	Wt.%				
HDPE-1	0	0	399	388	175	0.62
HDPE-2	0	0	402	387	183	0.64
HDPE-1F	2.08	12.78	394	380	132	0.48
HDPE-2F	1.55	9.52	399	380	150	0.52

[a] Here $(T_m)_{app}$ = apparent melting temperature.
[b] T_C = crystallization temperature.
[c] ΔH_a = apparent enthalpies of melting.
[d] $(1 - \lambda)_{\Delta H_u}$ = levels of crystallinity.

2.2. Synthesis and characterization

Functionalization reactions were carried out with diethylmaleate (DEM) in solution of orthodichloro benzene (*o*-DCB) and the initiator was 2-5-dimethyl-2,5(di-*t*-butyl) peroxihexane (DBPH). Reactions were carried out in a three-necked glass vessel equipped with a magnetic stirrer and by using nitrogen atmosphere in order to avoid polymer degradation.

Polyethylene was heated up to dissolve it in *o*-DCB, and when the polymer solution was completed, the temperature was raised up to 433 K and the DEM was added. Next, initiator solution in *o*-DCB was added and the mixture of the components was heated and stirred during the previously established reaction time. The vessel was then removed from the heating bath and the solution was poured onto cool acetone, maintaining stirring during the precipitation process. The polymer was washed in an excess of acetone and the resulting solid was finally dried under vacuum at 333 K. Under these conditions, it was possible to achieve the functionalization of HDPE with DEM avoiding crosslinking and degradation processes of the starting material [33].

For the characterization of the functionalized samples, infrared analysis and ^{13}C NMR techniques were used. FTIR spectra were obtained using a Nicolet 520B spectrometer after 20 scans at a resolution of 2 cm^{-1}. Films for FTIR were compression molded at 438 K and 300 kg/cm^2, during 4 min and were immediately cooled with dry ice.

The grafted DEM in the samples was determined by using calibration curves for the system reported recently [33]. Moreover, the analysis of the spectra obtained by both techniques demonstrated that the functionalization occurs by isolated units of DEM without detecting oligomers of DEM, either linked to the chain or homopolymerized. It has also been suggested in a previous work [34], that there is a preferred tendency in the chemical reaction to graft the DEM in the vinyl ends of the chain. The degree of functionalization of the samples studied in this work is shown in Table 2.

2.3. Thermal characterization

Melting temperature were determined in a Mettler TA-4000 DSC calorimeter, calibrated with indium. The HDPE samples (10–12 mg) sealed in an aluminum pan, were submitted to the following steps: heating the sample at 10 K/min from room temperature to 433 K and, after 5 min at this temperature, cooling at 10 K/min from this temperature to 253 K; finally, the sample is heated at a rate of 10 K/min from 253 to 433 K.

Enthalpies of melting were converted to levels of crystallinity, $(1 - \lambda)_{\Delta H_u}$, from the ratio $\Delta H_a/\Delta H_u$ being ΔH_a and ΔH_u the apparent and the completely crystalline heats of fusion, respectively; for the enthalpy of a polyethylene crystal, ΔH_u, the value of 69 cal/g was taken. The thermal parameters of the HDPE samples studied in this work are shown in Table 2.

2.4. Small angle X-ray scattering measurements

Small angle X-ray (SAXS) diffractograms were obtained using synchrotron radiation at the polymer beam line at HASYLAB (DESY, Hamburg). The beam is monochromatized (1.5 Å) by Bragg reflection at a Germanium single crystal which is bent in order to focus the beam in the horizontal direction. For focusing in the vertical direction a mirror was used. The scattering was detected by means of a linear Gabriel detector. Further details concerning the instrument can be found elsewhere [35]. Samples for SAXS measurements were prepared by compression molding at 438 K followed by a quenching in dry ice. The long period, *L*, was determined from the maximum of the SAXS curve.

2.5. Dynamic mechanical experiments

Dynamic mechanical experiments, DMA, were performed on a TA Instruments DMA 983 working in the flexural bending deformation mode at frequencies ranging from 0.05 to 3 Hz. The experiments were performed in the temperature range from 123 to 393 K, using a heating rate of 5 K/min. The samples (12 × 8 × 0.6 mm) were prepared by

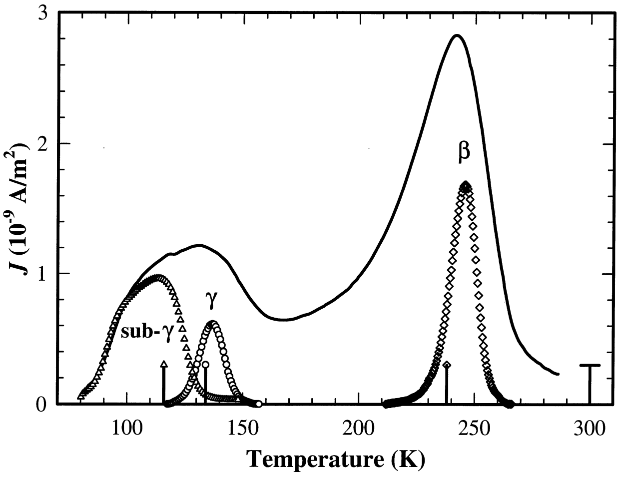

Fig. 1. TSDC spectra ($T < 300$ K) for HDPE-1F functionalized with 12.8% in weight of diethylmaleate groups: (—) complex spectrum; (open symbols) partially discharged spectra. The polarization temperatures are indicated with the respective symbols, $V_p = 1500$ V.

compression molding at 438 K followed by a quenching in dry ice. The thermally treated samples were annealed under vacuum at 368 K for 24 h.

2.6. TSDC experiments and computer analysis

Films for the TSDC experiments were compression molded at 438 K and immediately cooled in dry ice. Disks, 20 mm in diameter and 0.1 mm thick were cut and placed in the measuring cell designed in our laboratory and described elsewhere [22]. Sapphire disks 20 mm in diameter and 0.25 mm thick were intercalated between the polymer film and the metallic electrodes. The applied voltage was 1500 V unless otherwise specified. The temperature range explored here goes from 80 to 380 K and the heating rate, *b*, was 6 K/min. Complex spectra were recorded after polarizing at high temperatures. The various relaxation processes present in these complex spectra could be isolated by choosing the polarization temperature around the temperature of the maximum of the corresponding TSDC peak and by partially discharging the contribution of the lower temperature modes. If precise information on the enthalpy and entropy parameters of each relaxation process is sought, the whole profile has to be fitted and the simple Debye model is not adequate as the experimental curves will always be too broad as compared to the predictions of a single-valued relaxation time process. The Direct Signal Analysis, DSA, or the Simulated Annealing Direct Signal Analysis, SADSA, are fitting procedures recently introduced and discussed in great details elsewhere [36,37]. The basic idea is to decompose the complex profile in *N* elementary curves (labeled energy bins), whose characteristic reorientation energies are equally spaced in a chosen energy interval. The expression for the depolarization current density, $J_D(T)$, is now given by,

$$J_D(T_j) = \sum_{i=1}^{N} \frac{P_{0i}}{\tau_i(T_j)} \exp\left[-\frac{1}{b} \int_{T_0}^{T_j} \frac{dT'}{\tau_i(T')} \right],$$

$(j = 1, m;\ N \leq m)$

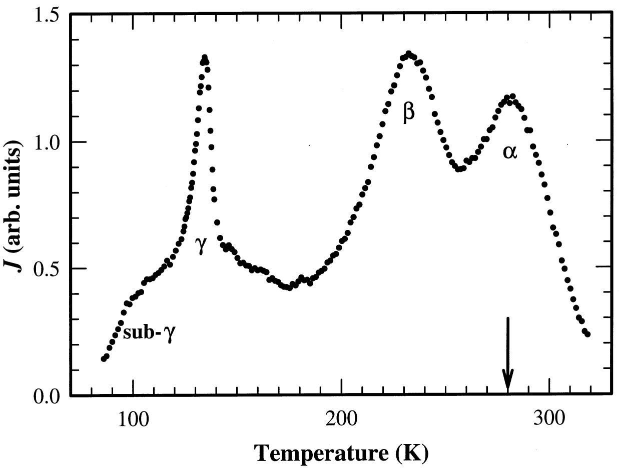

Fig. 2. TSDC spectrum for LLDPE functionalized with 1.9% in weight of diethylmaleate groups. $T_p = 280$ K.

The curve fitting procedure will find the best combination of the *N* components contribution to the total polarization, P_{0i}, and of the pre-exponential factors, τ_{0i}, corresponding to each energy bin. These parameters will fully characterize the relaxation times distribution, RTD, describing each mode, provided that the temperature dependence of the relaxation times is assumed. For the sub-T_g modes in polymers the Arrhenius law,

$$\tau(T) = \tau_{0i}\exp(E_{0i}/kT)$$

is found to be satisfactory in the description of localized reorientations which do not involve main chain motions. At $T \geq T_g$ the Vogel–Tammann–Fulcher expression, VTF, or its equivalent the Williams–Landel–Ferry dependence is to be used as many previous experimental works have shown [38]; this expression has received a theoretical justification by using either the free volume concept or statistical mechanics [39]. A VTF energy and pre-exponential factor can be introduced if the VTF relaxation time is written as:

$$\tau(T) = \tau'_{0i}\exp(E'_{0i}/k(T - T_0)),$$

where T_0 is the VTF temperature where all the chain motions are frozen in the sample. The DSA and the SADSA codes will perform the whole profile fitting by using either a non-linear least squares Marquardt–Levenberg algorithm, or the simulated annealing Monte Carlo procedure which is more reliable as the parameters space is explored randomly and the absolute minimum of the function to minimize is more securely reached [37].

3. Results

The experimental results given by the different

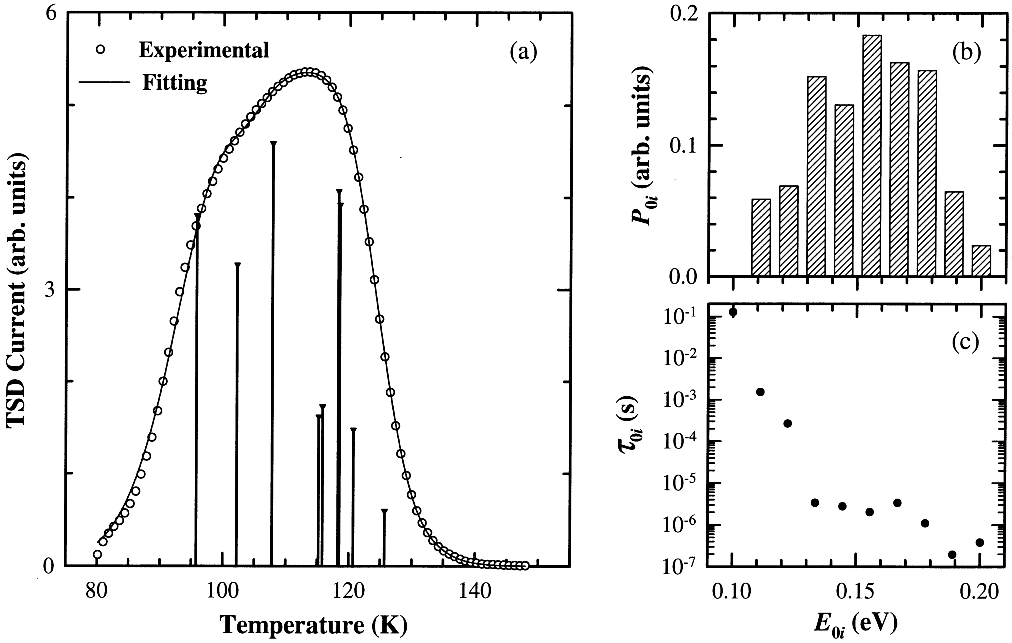

Fig. 3. Results of the DSA for the sub-γ relaxation for HDPE-1F with Arrhenius relaxation times: (a) experimental and fitted profile; (b) energy histogram; and (c) variation of τ_{0i} with the energy bin value.

techniques used in this work will be compared in order to understand the relaxation behavior of this material both from the dielectric and the mechanical point of view.

3.1. TSDC results

Fig. 1 shows the complex low temperature TSDC spectrum ($T < 300$ K) for the polyethylene with the higher degree of functionalization, HDPE-1F, polarized at 300 K. This complex spectrum shows a multicomponent γ-region and a more intense β-peak. In a previous study [22] on LLDPE, also functionalized with diethylmaleate, the experimental trace clearly showed the existence of a sub-γ, and γ modes in this same low temperature region as seen on Fig. 2. In the HDPE the γ-peak is less visible than before, its intensity being similar to that of the sub-γ peak,

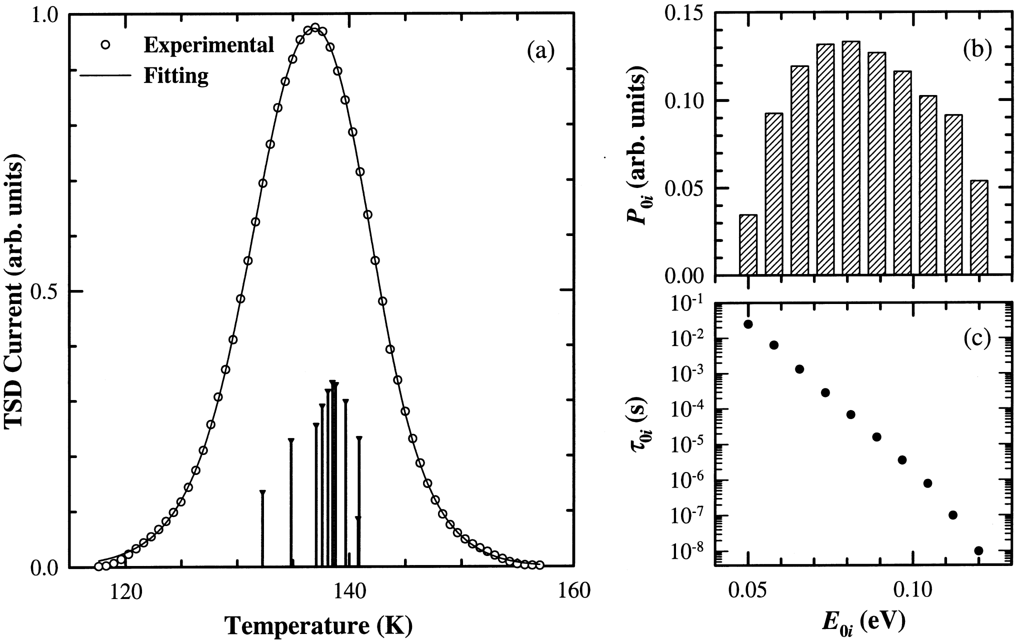

Fig. 4. Results of the SADSA for the γ-relaxation for HDPE-1F with VTF relaxation times: (a) experimental and fitted profile; (b) energy histogram; and (c) variation of τ_{0i} with the energy bin value, $T_0 = 67.7$ K.

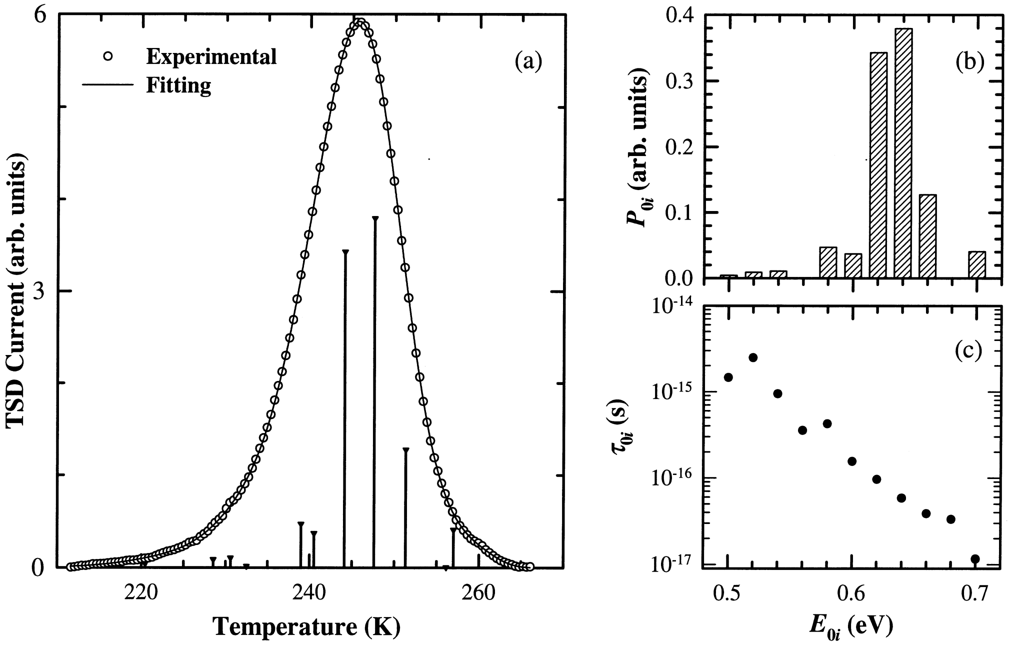

Fig. 5. Results of the SADSA for the β-relaxation for HDPE-1F with VTF relaxation times: (a) experimental and fitted profile; (b) energy histogram; and (c) variation of τ_{0i} with the energy bin value, $T_0 = 67.7$ K.

but it can still be separated by carefully choosing the polarization conditions and partially discharging the low temperature components of this complex peak. The clean curves obtained after these cleaning procedures and labeled sub-γ, γ and β, are also shown in Fig. 1 for the HDPE-1F. The polarization temperatures used here are 116, 134 and 238 K respectively. The maxima of these peaks are located at 116, 137 and 245 K. Sample HDPE-2F with a different comonomer and less DEM (see Table 1.) shows a qualitatively similar TSDC spectra.

The DSA for the three components shown in Fig. 1 are presented in Figs. 3, 4 and 5; they include the experimental and DSA fitting results (a), the energy histogram which represents the contribution to the total polarization from each energy bin (b), and the variation of the pre-exponential factor, τ_{0i} for each elementary contribution (c). The sum of square residuals for the normalized curves [36], χ^2, is always lower than 2×10^{-7}. It is to be noted that Arrhenius relaxation times were used for the fitting procedure of the sub-γ mode whereas Vogel–Tammann–Fulcher temperature dependencies have to be used for the fitting of the γ and β-transitions. The T_0 values obtained from the two independent fittings are the same and equal to 67.7 K.

The high temperature TSDC spectrum ($T > 300$ K) of HDPE-1F consists of a very intense peak labeled as the α-relaxation which is shown in Fig. 6 together with the lower temperature relaxations. In the HDPE functionalized samples the α-relaxation occurs at much higher temperature than it was previously reported in LLDPE samples, see Fig. 2, and its intensity as compared to the β-relaxation has steeply increased.

Fig. 7 shows the usual format for the DSA results for the α-mode, also performed with VTF relaxation times. The best T_0 values which are also adjusted during the fitting procedures are found to be the same, 67.7 K, for the three relaxations (γ, β and α) analyzed here by using VTF relaxation times; this is expected for a parameter which indicates the temperature where all the molecular motions are frozen and should be characteristic of the polymer.

3.2. DMA results

Fig. 8 shows the variation of the loss modulus, E'', recorded at 0.1 Hz as a function of temperature for

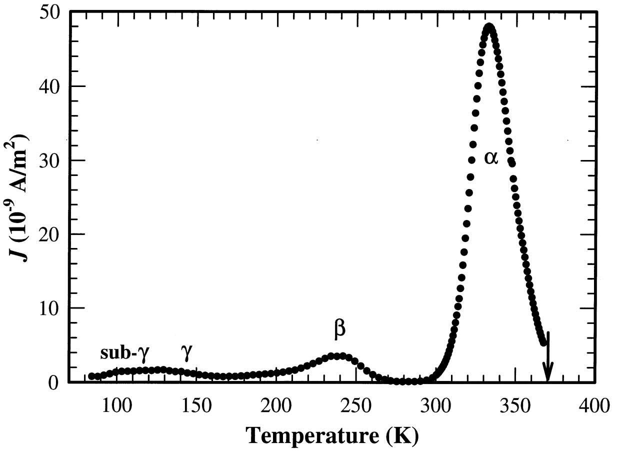

Fig. 6. TSDC spectrum for HDPE-1F for 80 K $< T <$ 370 K, $T_p = 371$ K and $V_p = 1500$ V.

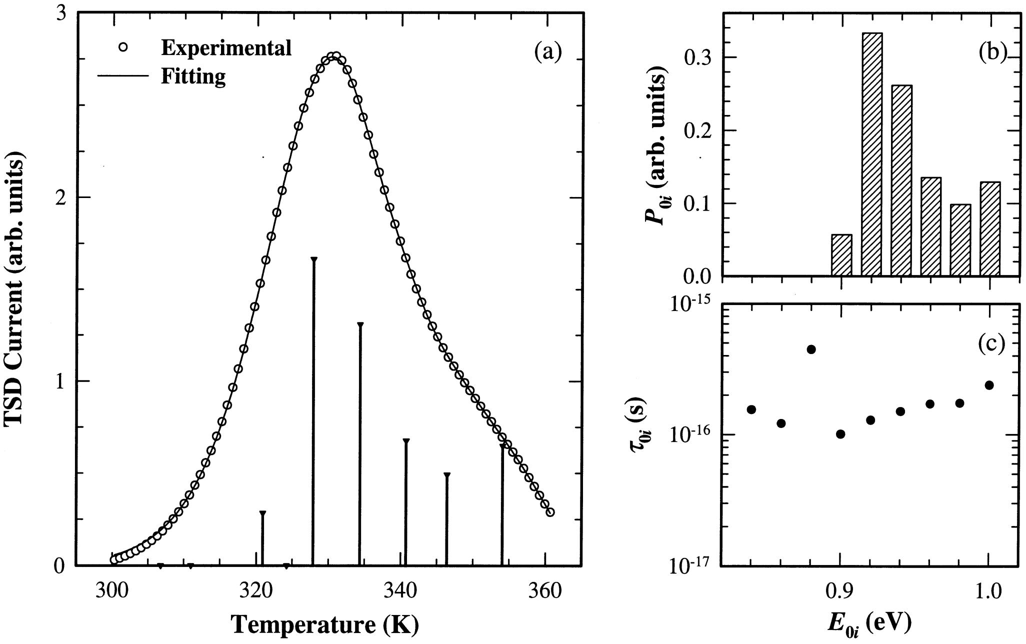

Fig. 7. Results of the SADSA for the α-relaxation for HDPE-1F ($V_p = 1500$ V) with VTF relaxation times: (a) experimental and fitted profile; (b) energy histogram; and (c) variation of τ_{0i} with the energy bin value, $T_0 = 67.7$ K.

HDPE-1, with 0.8% mol of cohexene (see Table 1), and samples using the same starting polyethylene with increasing degrees of functionalization. The highest DEM content corresponds to HDPE-1F sample which TSDC results were presented in the above section. The unfunctionalized sample shows clearly a low temperature relaxation at 159 K, i.e. in the γ-region, and a broad band at 300 K with a shoulder in the 223–273 K zone; these relaxation modes are labeled γ, β and α with increasing temperature. As the DEM content increases, the γ-peak shifts to lower temperature, an intense peak grows and sharpens around 272 K, while the shoulder on the high temperature tail decreases in intensity. In order to identify the β and α-relaxations in the functionlized polyethylenes, samples with the highest DEM content were thermally treated in order to increase the lamellar thickness; the samples were annealed at 368 K for 24 h under vacuum. The DMA spectra of the treated samples show a broadening of the intermediate intense relaxation accompanied by an increase and a better resolution in the high temperature shoulder which indicates that the latter should be assigned to the α-relaxation which is the mode repeatedly reported as sensitive to the lamellar thickness. These features are independent of the type of comonomer whether it is hexene or butene.

4. Discussion

In order to identify the specific molecular motions that originate the observed relaxation modes in functionalized HDPE, the comparison with the results obtained in LLDPE grafted with the same polar group [22] may be helpful. The LLDPE previously studied had a higher comonomer content (3% mol butene) and a much lower DEM content (1.9% in weight as compared to 12.8% for the samples used in the

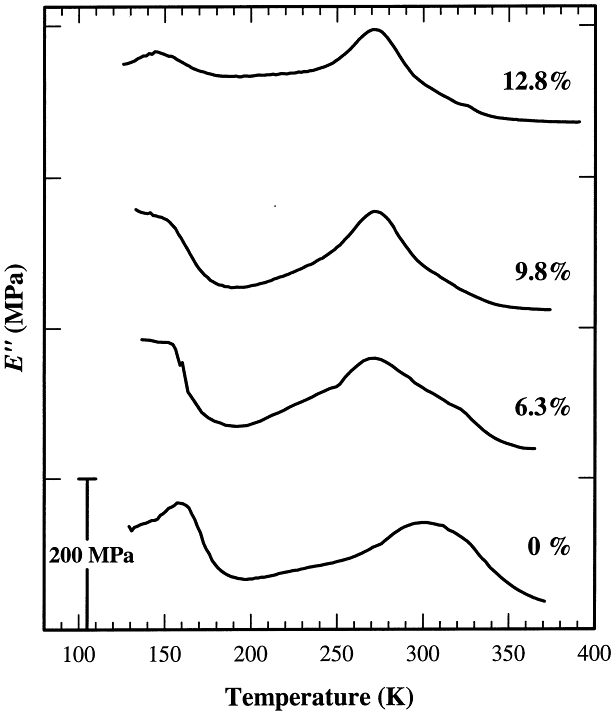

Fig. 8. Variation of the mechanical loss modulus as a function of temperature at 0.1 Hz, for increasing values of the DEM content (% in weight).

present study). The resulting crystallinities range from 30% in the LLDPE to about 50% for the HDPE-F samples. These structural differences are reflected in the changes observed in the relaxation spectra of the polyethylenes studied in this work as compared to the LLDPE.

The different relaxations will be discussed separately as a function of type and content of comonomer, degree of functionalization, crystallinity and lamellar thickness.

4.1. Sub-γ and γ modes

In Fig. 2 the LLDPE complex TSDC spectrum is plotted and the multicomponent character of the low temperature mode is clearly noted. This band was separated in two components namely a broad sub-γ mode assigned to local motions of the polar groups, and the narrow and intense γ-peak, which was assigned to the dielectric manifestation of the primary glass transition of the material [22]. This conclusion was reached after the cleaning procedure was performed and allowed the separation in two components with different temperature dependencies for the relaxation times used in the DSA procedure, i.e. Arrhenius and VTF for the sub-γ and γ-mode, respectively. This multicomponent character for the low temperature relaxation had been previously reported in LPE by Stehling and Mandelkern [28] by DMA and interpreted as two overlapping relaxations arising from the non-crystalline domains of the polymer. The shapes of these DMA curves were strikingly similar to the TSDC of LLDPE. The γ-transition observed by DMA was assigned to the glass transition of linear polyethylene by these authors based on thermal expansion, calorimetric measurements, in addition to DMA experiments as a function of the crystallinity level. Recently, Alberola et al. [16,17] by using high-resolution mechanical spectrometry, demonstrated that the observed features of the γ-transition in linear and branched polyethylenes such as structural recovery after physical aging at $T < T_\gamma$, and WLF dependencies, are characteristic of the primary glass transition.

The TSDC trace shown in Fig. 3(a) for the sub-γ mode of HDPE-1F presents a similar shape as compared with LLDPE, but some differences in the energy distribution are observed. The energy histogram is broader and centered at slightly higher energy (+0.02 eV) for HDPE-1F. These quantitative results indicate that the localized motions of the DEM groups responsible for this sub-γ mode are more restrained in the HDPE samples due to the significant higher DEM content and to the higher crystallinity level.

The γ-transition isolated by the partial discharge procedure shown in Fig. 1 is far less visible than in the LLDPE sample; an intensity decrease is to be expected due to the less abundant amorphous regions in the HDPEs; however, the magnitude of the reduction is larger than expected. This may indicate that the polar groups are less abundant in the amorphous zones whose motion gives rise to the γ-relaxation. The concentration of the DEM groups should then be higher in other regions such as for example in the amorphous-crystalline interface. The energy distribution shown in Fig. 4 for the γ-mode is shifted to lower energies and much narrower than the one found in LLDPE thus indicating a more homogenous material relaxing at T_γ which agrees with the lower comonomer content in these polymers. The observed linear dependence of the pre-exponential VTF factor as a function of the energy shows the existence of a compensation law [40,41] pointing to the same molecular origin.

A similar lowering in the intensity for the γ-relaxation is also observed in the DMA spectra obtained for the functionalized HDPE when compared with the well resolved peak in the unfunctionalized sample as seen in Fig. 8. This figure also shows the shoulder in the low temperature tail which can be related to the sub-γ transition reported by Stehling and Mandelkern [28] and Laredo et al. [22]. Additionally, the observed shift to lower temperature observed by DMA with increasing DEM content, can be explained by the decrease in crystallinity in these samples as measured by DSC (see Table 2).

4.2. β modes

The DMA spectra plotted in Fig. 8 show the growth of a peak at intermediate temperatures when the DEM content increases, thus the idea that branching enhances the intensity of the β-transition in ethylene copolymers [12,13] is confirmed and its origin related to the segmental motions of chains located at the interfacial regions. In the unfunctionalized HDPE the β-peak appears as a broad shoulder in the vicinity of 233 K originated by the comonomer at the interface. As the DEM content increases this shoulder coexists with a narrower peak at 272 K that is obviously related to the presence of the polar groups besides the ethyl or butyl branches. The β-relaxation observed by TSDC also shows a long tail on the low temperature side, which could then be related to the motion of the dielectric probes that are located near these branches. Moreover, the energy histogram presented in Fig. 5 for the cleaned β-relaxation shows a narrower energy histogram than that found for the LLDPE, which was a more inhomogeneous material due to its higher comonomer content.

It is to be remarked that all the TSDC transitions already reviewed occur at lower temperatures than the corresponding DMA peaks as expected for experiments which are performed at lower frequency, i.e. 10^{-3} Hz (equivalent frequency for the TSDC runs) vs. 0.1 Hz for the E'' measurements.

4.3. α relaxation

The existence of this relaxation has been widely confirmed and its behavior as a function of the key structural factors which describe the semi-crystalline state exhaustively studied [12]. Its location in temperature is determined primarily by the crystallite thickness and not by the degree

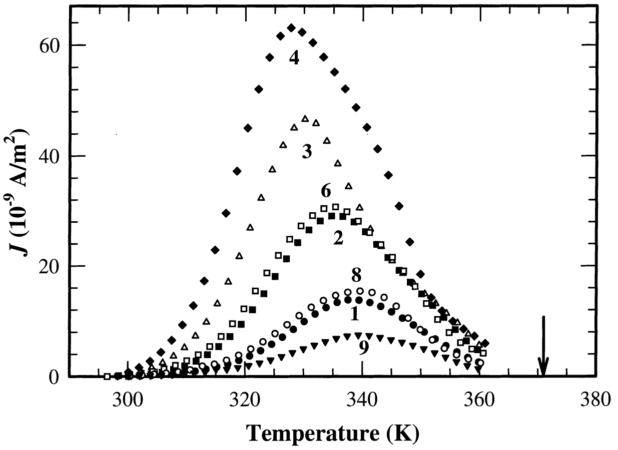

Fig. 9. Variation of the TSDC α-peak for HDPE-1F with the applied voltage, the numbers indicate the experiments sequence: 1(●) 500 V; 2(■) 1000 V; 3 (△) 1500 V; 4 (◆) 2000 V; 6 (□) 1000 V; 8 (○) 500 V; 9 (▼) 250 V.

of crystallinity or the supermolecular structure. It is generally accepted that the α-relaxation is originated by the motions in the interface that can be coupled to the mobility of chains within the crystallites. In the functionalized HDPE with DEM, the FTIR experiments and the study of the depression of the melting temperature as the DEM content increases, indicated that the polar groups are not randomly located along the chain but preferentially grafted on the end vinyl groups [33,34]. Due to the bulkiness of these polar groups they are excluded from the crystallites and would accumulate at the crystal boundaries creating an enriched DEM zone at the interfaces. As the DEM groups are the dielectric probes for a TSDC experiment, this technique is going to be very sensitive for the detection and study of the α-relaxation. On the contrary, the DMA spectrum for different grafting degrees shows a decrease in the intensity of the α-relaxation and a predominance of the β-relaxation as it has been also observed in ethylene copolymers [11,13]. The increase in the branch amount results in an increase in the interfacial material, a lowering of the crystallite thickness and to shorter sequences of ethylene units.

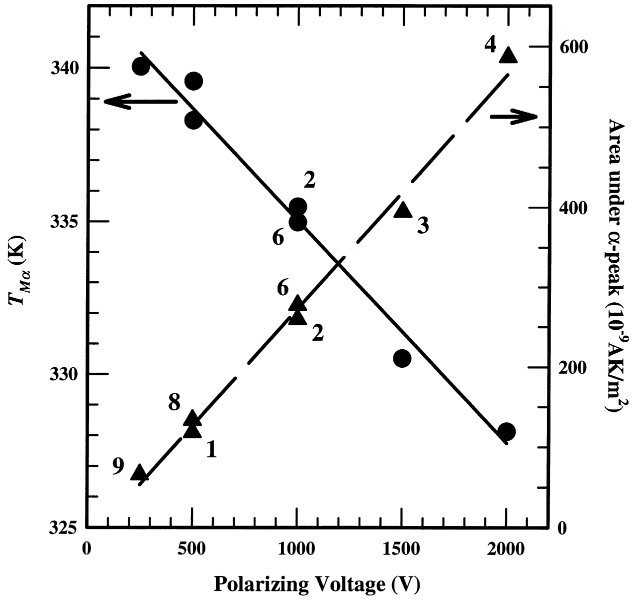

Fig. 10. Variation of the temperature of the maximum of the α-peak (left Y-scale), and of the area under the peak (right Y-scale), for HDPE-1F with the applied voltage. The numbers indicate the experiments sequence.

In Fig. 8 it is readily observed that on going from the unfunctionalized HDPE-1 to the highest grafted material, HDPE-1F the α-relaxation decreases drastically and shifts to lower temperatures as a consequence of the decrease in the crystallite thickness and the growth of the interfacial zone. In order to estimate the crystallite thickness of these samples, a SAXS study using synchrotron radiation has been carried out at room temperature as indicated in the Experimental section. The scattered intensity, after Lorentz correction, was plotted as a function of the scattering vector $s(s = (2\sin\theta)/\lambda)$, λ being the wavelength and θ the scattering angle. The obtained patterns show a maximum originated by the density differences due to the alternation of crystal and amorphous regions with rather uniform thickness. The long period represents the periodicity of the sum of the crystalline and non-crystalline thickness which is obtained from the maximum of the SAXS curve as $L = 1/s_{\max}$. The long spacings estimate for HDPE-1 and HDPE-1F are 180 and 150 Å respectively, indicating a decrease in the crystalline thickness with functionalization, and correlates well with the DMA results. These DMA results can only be compared with those previously reported on ethylene copolymers [12,13] as the effect of DEM or similar polar groups are not available to the best of our knowledge.

Referring now to the TSDC results in the most highly grafted material shown in Fig. 6, the highest temperature peak shows very interesting features. Its intensity is 8 times larger than that of the β TSDC peak and its position in HDPE is considerably shifted to higher temperatures as compared to LLDPE. As the lamellar thickness should be larger in the first case, even though the total branching content is similar, the DEM distribution and the low comonomer content in the HDPE favors longer ethylene sequences than in the highly branched lowly grafted LLDPE. However, the position of this high temperature peak as compared to the α-mechanical relaxations is located at higher temperature than expected if the frequency difference is taking into account. This is not the case for the lower temperature relaxations discussed in the previous sections. Moreover, the DSA results on this high temperature peak presented in Fig. 7 show also significant differences with the DSA analysis of the γ and β-peaks. First, the energy distribution is much narrower and there is no indication of the existence of a compensation law at this high temperature, as the τ_{0i} remain almost constant for the significant bins of the

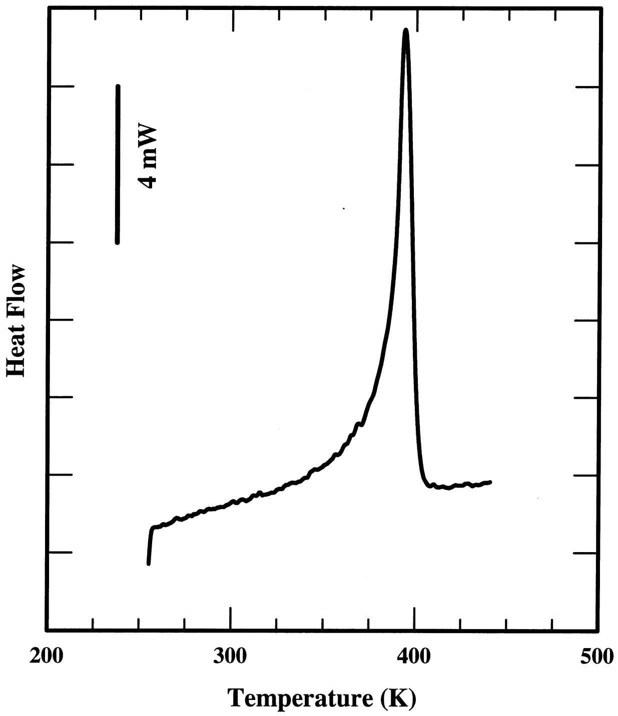

Fig. 11. DSC curve for HDPE-1F at a heating rate of 10 K/min.

energy histogram. Reorientation processes fundamentally different from those discussed for the lower temperature relaxations must then originate this high temperature relaxation.

In order to check the proportionality between the polarizing voltage and the area under the TSDC α-curve, a series of identical experiments was carried out using the same polarizing temperature, $T_p = 371$ K, and thermal cycles, varying only the applied voltage from 250 to 2000 V. The recorded spectra are shown in Fig. 9, the numbers indicating the sequence of the TSDC runs; the open symbols correspond to check runs at 1000 V (6th run) and 500 V (8th run). As can be easily observed in this figure the α-peak shifts to lower temperatures as the voltage is increased, while the area under the curves grows linearly, both variations are plotted in Fig. 10. The other relaxations in the TSDC spectrum behave normally, i.e. the peaks do not shift and the area under the curves as well as the height of the peaks are proportional to the applied voltage. It is to be noted that the polarization step in the TSDC experiment implies to rise the sample temperature to a point where melting of the most imperfect crystals is expected as shown in the thermogram presented in Fig. 11. In order to check whether successive thermal TSDC cycles would change the crystallinity, lamellar thickness, interfacial structure and other structural parameters that may affect the α-reorientation process, experiments were repeated in order to check if the thermal history alone was affecting the results. The reproducibility observed in Figs. 9 and 10 between the 1st and 8th run at 500 V and the 2nd and 6th run at 1000 V excluded this possibility. The voltage is thus the determining parameter for the observed shift of the α-peak. If it is assumed that this high temperature peak is the dielectric manifestation of the reorientation process responsible for the α-mechanical relaxation, the polarizing voltage effect may be interpreted as a result of a variation of the lamellar thickening during the polarizing step in the presence of a strong applied field. As the crystals are metastable they tend to thicken at temperatures close to the original crystallization temperature. The presence of the electric field may affect the result of this annealing. As the field strength increases the lamellar thickening process will be less efficient; consequently, the peak will shift to lower temperatures. An alternate explanation could be to assign this high temperature peak to a process which is originated by the relaxation of the space charges trapped in the material. However, the linear response of the polarization as a function of the applied voltage, for voltages up to 2000 V applied to the sapphire disks-polymer arrangement, lead us to discard this possibility.

5. Conclusions

The dielectric and mechanical experiments reported here on HDPE functionalized with high amounts of DEM have allowed a better understanding of the origin of the relaxations detected on well characterized samples. The presence of the diethylmaleate groups allowed the dielectric characterization as they act as dipolar probes whose reorientation, through motions either localized or caused by the cooperative motions of the main chain, can be detected; the different modes can be isolated and their detailed study thus performed. The qualitative features of the TSDC spectrum are similar to those recorded in a previous study [22] from LLDPE samples with a much lower grafting degree (1.9% in weight to be compared with 12.8% for the present work), a higher molar comonomer amount and a lower crystallinity degree (30% instead of 48%). It is found that the lowest temperature TSDC peak, reported [22] as asymmetric before, is composed of a sub-γ component which has been assigned to localized motions of the DEM groups which obey Arrhenius relaxation times and whose reorientation energy ranges from 0.12 to 0.20 eV. In the HDPE the γ-mode is not the predominant one at low temperatures as it was in the LLDPE and the broad band had to be separated into its two components in order to clarify its existence. However, its assignment to the primary glass transition is confirmed here by the need to use VTF relaxation times for the precise fitting of the γ-peak profile, placing the T_g at 137 K for HDPE with a DEM content of 12.8% in weight. This relative decrease in intensity is attributed to the increase in crystallinity observed in the HDPE samples, and to the distribution of the DEM groups which are now preferentially located at the crystalline interfaces and not in the mobile amorphous phase whose motions originate the γ-transition. The T_0 parameter of the VTF relaxation time is found to be for the γ-mode equal to 67.7 K which is 2 K lower than the value found in the equivalent analysis in LLDPE. The γ-mode observed in HDPE by DMA shifts to lower temperature as a result of the decrease of the crystallinity as the grafting degree increases. The β-mode has also been successfully analyzed by using VTF relaxation times. Its intensity observed by DMA grows as expected with the increase in branching and in agreement with its assignment to segmental motions occurring in the interfacial regions. The pseudo glass transition character often assigned to this β-mode as due to the relaxation of disordered chains located near the crystalline interfaces is confirmed here, and it should be distinguished from the unrestrained molecular motions in the mobile amorphous phase which are responsible for the γ-mode.

The behavior of the mechanical α-mode as the branching increases which results in a shortening of the ethylene units and a decrease in the lamellar thickness and the high intensity of the dielectric manifestation of these reorientation processes, confirms that the important parameter is the crystallite thickness. Moreover, the 12 K shift to lower temperatures of the α-mode detected by TSDC as the polarizing voltage grows is a new experimental fact that has to be taken into account. If the shift to lower temperatures observed here is to be related to the reduction in the crystallite thickness then it must be concluded that the polarization step described above somewhat reduces this crucial characteristic extensively studied by Popli et al. [12] who report a 70 K negative shift on going from 150 to 50 Å in crystallite thickness. As the crystals are annealed at the polarizing temperature it may be assumed that the thickening process in the presence of an increasing applied field leads to smaller crystallites. This would mean that the chain motions occurring in these imperfect crystals are leading the reorientations of the chain belonging both to amorphous phase and lamellae which originate the α-mode. The defect diffusion along the molecular chains within crystallites [42,43] could cause some molecular motions in the amorphous phase. This picture would also explain the low intensity of the mechanical α-mode and the high intensity of the TSDC manifestation of the same process. The location of the DEM groups, preferentially grafted on the end vinyl groups, suggest an interfacial zone very rich in polarizable entities around the imperfect crystals; there, the defect diffusion originates the motion of the end of chains that are excluded from the crystals and free to move in the nearby interfacial zones.

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