# α-Relaxation/retardation mode in semicrystalline polymers with flexible chains

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The molecular mobility of two semicrystalline polymers with flexible chains—chemically crosslinked low density polyethylene (XLPE) and poly(vinylidene fluoride) (PVDF)—has been investigated in the temperature range between room temperature (above their glass transition temperature) and their melting point. D.s.c. was used to characterize the conformational evolutions related to crystalline domains. Thermostimulated currents and creep were used to study the dynamics of these movements. For both polymers, the α-relaxation/retardation mode is located in the temperature range of a small endothermic phenomenon. These low temperature d.s.c. peaks are not related to any melting process but rather to conformational disorder in the crystal–amorphous interphase. The fractional polarization/stress technique was applied to obtain the distribution of relaxation/retardation times. A compensation phenomenon was found above the α-relaxation mode of β-PVDF and XLPE. It has been ascribed to conformational movements associated with an order–disorder phase transition in the vicinity of the melting point. These high temperature phases would correspond to the paraelectric phase of β-PVDF and to the hexagonal phase of XLPE. Insofar as the α-mode is liberating molecular mobility at the crystal–amorphous interphase, it appears as a precursor of the order–disorder transition.

**(Keywords: molecular mobility; semicrystalline polymers; flexible chains)**

## INTRODUCTION

In the last decade, several new concepts have been introduced to describe the structure of semicrystalline polymers, especially for modelling the interphase layer, and the general ordering of the crystal. Concepts like conformation disordered (condis) crystal[1] and, more recently, transient phases[2,3] have been introduced since molecular dynamics, Raman and i.r. spectroscopies and small angle X-ray scattering[4] have been applied to polymer research. These approaches are especially adapted to the analysis of solid–solid transitions in crystalline solids[2,3].

Spectroscopic experiments cannot be applied directly to the investigation of low frequency molecular motions liberated at the glass transition temperature ($T_g$) because the time of observation is too fast compared with the characteristic time of molecular mobility. Dielectric and mechanical spectrometries have been among the most used techniques for the study of molecular motions liberated at the $T_g$ in polymers. However, relaxation/retardation modes generally consist of a distribution of relaxation/retardation times, and their resolution is complex.

During the past two decades, thermally stimulated currents (TSCu) and creep (TSCr) have been applied successfully to the study of such molecular mobility in polymers[5–8]. The advantages of thermostimulated techniques are their low equivalent frequency ($\approx 10^{-3}$ Hz), and the possibility of the experimental resolution of complex modes. The thermostimulated techniques were applied successfully to the measurement and the characterization of the anelastic effects associated with the glass transition. In addition, the resolution of overlapping energy loss peaks frequently found in broad secondary relaxations is allowed.

Poly(vinylidene fluoride) (PVDF) and polyethylene (PE) have been chosen as models for this study. PVDF is an interesting polymer with respect to its electroactive properties. In PVDF, several polymorphic structures have been identified[9]. The most important ones are the α-phase, with a *TGTG′* conformation, and the β-phase with an all-*trans* conformation. The latter is polar and it induces the ferroelectricity of PVDF[10]. It is obtained from films initially in the α-phase by stretching at a ratio of 300/400%.

Low density polyethylene (LDPE) is often chosen as a model for the description of the crystallization mechanisms and the structure and morphology of polymer crystals[11,12]. In spite of its complexity, crosslinked low density polyethylene (XLPE) is more suited for the study of high temperature relaxations, because of its high thermal and geometrical stability. Although the existence of a crosslinked network affects the crystallization mechanisms[13], its mechanical relaxation response is similar to that of LDPE[14].

PVDF and XLPE have analogous chemical structures: both are symmetrically substituted, and H and F atoms

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have similar atomic radii. Additional common features in these polymers are the moderate degree of crystallinity ($\approx 50\%$), and their low $T_g$ value ($< -30$°C), so that the amorphous phase is in a liquid-like state at room temperature. At least three relaxation/retardation modes ($\alpha, \beta, \gamma$) have been found in these polymers. It was proposed that they have the same phase origin in PVDF and XLPE[15]. The $T_\alpha$ values for PVDF and XLPE are located around 40 and 60°C, respectively. They are associated with the crystalline phase[16].

In this work, we will focus on the temperature range of the α-mode, and above (20°C, 200°C). Special attention will be paid to the molecular mobility of the amorphous phase in these flexible semicrystalline polymers. Many studies have been devoted to this subject[17,18] but, up to now, there has been no definitive assignment. The main purpose of this work is to investigate the molecular mobility liberated above the $T_g$ in flexible semicrystalline polymers. A comparative study of transitions and α relaxation and retardation modes in PVDF and XLPE has been performed by means of d.s.c., TSCu and TSCr spectrometries.

## MATERIALS AND METHODS

### *PVDF*

The samples used in this study were PVDF films (40 μm thick) supplied by Solvay & Co. α-PVDF and bioriented β-PVDF were investigated. Their molecular weight is $\sim 2 \times 10^5$.

### *XLPE*

A peroxide XLPE was investigated. The degree of crosslinking and the molecular weight between crosslinks for XLPE were determined by using the solvent extraction technique.

The boiling xylene method utilized by Kao and Phillips[13] was chosen. Polyethylene samples were subjected to extraction over 72 h in boiling xylene (138°C). The molecular weight between crosslinks was determined by linear swelling in xylene at 100°C over 24 h. The extractable percentage (or sol fraction) was 17.5% and the molecular weight between crosslinks was $1.5 \times 10^4$.

### *D.s.c.*

The d.s.c. thermograms were recorded on a Perkin–Elmer DSC-7. Samples (15–20 mg) were enclosed in aluminium pans. The scanning rate was 10°C min$^{-1}$ and the temperature range used was 0–200°C. These experiments allowed us to determine the transition spectra from 0 to 200°C.

### *TSCu (TSCr)*

TSCu and TSCr spectrometries were applied to characterize relaxation phenomena in PVDF and XLPE, respectively. TSCu was used for PVDF as it is polar. Since XLPE is non-polar, mechanical spectrometry is more adequate. Consequently, the retardation phenomena of XLPE were characterized by TSCr spectrometry.

The principle of TSCu (TSCr) is the following: the sample is submitted to a static electric field (or mechanical stress) for 2 min at a temperature $T_p$ (or $T_\sigma$) allowing the mobile units of the polymer to orientate. This out-of-equilibrium configuration is then 'frozen-in' by a rapid quench to a temperature $T_0$ much smaller than $T_p$ (or $T_\sigma$) where any molecular motion is hindered, and the electrical (or mechanical) stress is removed. The return to equilibrium of the sample is induced by a controlled increase of the temperature (7 K min$^{-1}$). The mobile units relax. The dielectric (or mechanical) recovery, polarization $P$ (or strain $\gamma$), its time derivative, and the temperature are recorded *versus* time. The time derivative of the polarization $P$ (or strain $\gamma$) recovery *versus* temperature constitute the TSCu (or TSCr) spectra.

In polymers, the dielectric and anelastic responses are generally described by making the assumption of a distribution of relaxation/retardation times. The great advantage of the TSCu (or TSCr) techniques is that they allow us to perform a detailed study of this distribution. By applying the technique of fractional stresses[5–8] in TSCu (or TSCr) experiments, the complex spectrum can be resolved experimentally into elementary spectra. The usual cycle to obtain the complex spectrum, but with a narrow temperature window when applying stress, allows us to obtain elementary spectra.

## RESULTS

### *Transition spectra*

*Figures 1* and *2* show the variation of the heat capacity of β-PVDF, $\Delta C_p$, in the temperature range 25–200°C, obtained upon heating and cooling at a scanning rate of 10 K min$^{-1}$. (Note that the $\Delta C_p$ scale between 25°C and 100°C has been magnified ten times.)

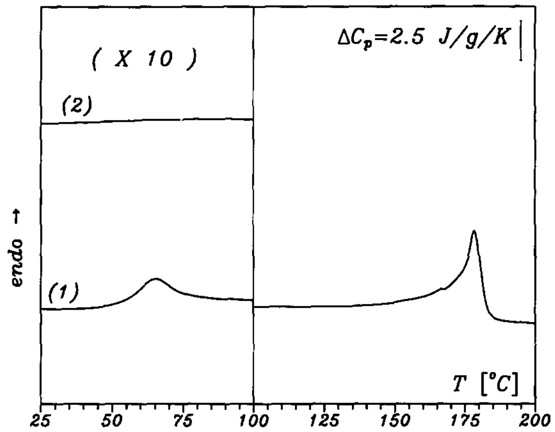

**Figure 1** D.s.c. thermogram of β-PVDF upon heating at 10°C min$^{-1}$: (1) as-received sample; (2) second heating after slow cooling

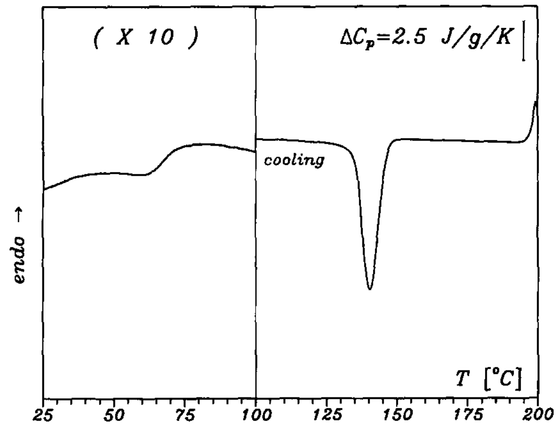

**Figure 2** D.s.c. thermogram of β-PVDF upon cooling at 10°C min$^{-1}$

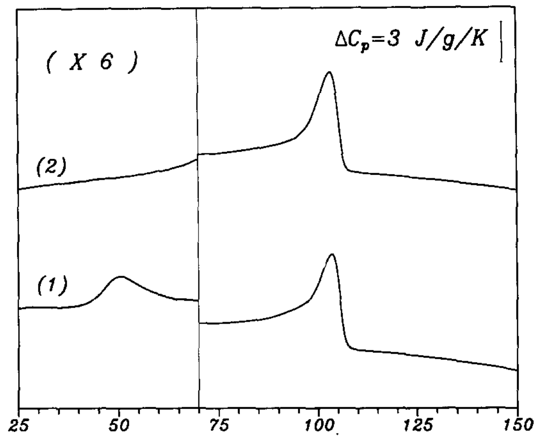

**Figure 3** D.s.c. thermogram of XLPE upon heating at 10°C $\mathrm{min}^{-1}$: (1) as-received sample; (2) second heating after slow cooling

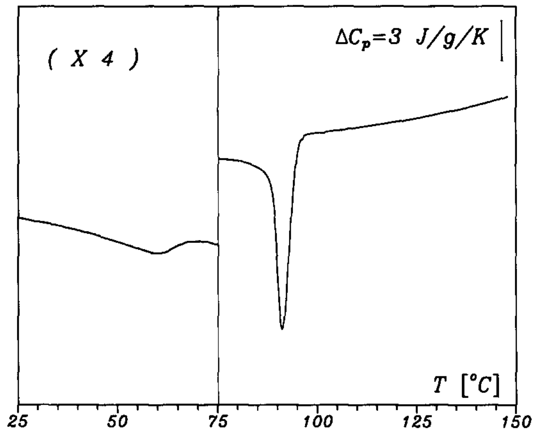

**Figure 4** D.s.c. thermogram of XLPE upon cooling at 10°C $\mathrm{min}^{-1}$

Two endothermic peaks appear in the first heating cycle (*Figure 1*). The higher temperature peak (174°C) corresponds to the melting of crystallites. The peak located at ~60°C is obtained only in the first heating cycle, i.e. it does not occur on thermograms recorded immediately after the first cycle (second heating; *Figure 1*). It should be noted that annealing at room temperature for 24 h makes it reappear. We have previously shown[19] that this phenomenon occurs for both α- and β-PVDF polymorphs.

Upon cooling from the melt (*Figure 2*), crystallization occurs at 140°C. An exothermic peak is found at 63°C, i.e. close to the low temperature endothermic peak found upon heating. It occurs in the cooling cycle only if the sample is previously in the molten state: it was not observed upon cooling from a temperature lower than the melting temperature.

Under the same experimental conditions as for PVDF, thermograms of XLPE show two transitions upon heating as well as upon cooling (*Figures 3* and *4*). The higher temperature peaks, respectively, correspond to melting ($T_m = 100$°C) and crystallization ($T_{cr} = 80$°C). The lower temperature peaks have the same behaviour as in PVDF: the endothermic peak in the first heating thermogram disappears in the second scan obtained immediately after crystallization (*Figure 3*). In the cooling cycle from the molten state (*Figure 4*), a low temperature exothermic peak is also observed.

In a classical melting/crystallization process in semicrystalline polymers, $T_m$ is always located above $T_{cr}$, with the lag depending on the size of the crystallites[20]. In our case there is no clear relationship between the temperature position of the exothermic and endothermic low temperature peaks. In PVDF the lag is nearly zero, and in XLPE, the low temperature exothermic peak is above the corresponding endothermic peak. These observations show that the low temperature exothermic peak is not due to the melting of small crystallites that would have been segregated during the main crystallization.

### *Relaxation/retardation spectra*

*Figure 5a* shows the TSCu spectra obtained in α- and β-PVDF after polarization at $T_p = 80$°C under an electric field of 5 MV $\mathrm{m}^{-1}$ over 2 min. The peak located at $T_m = 50$–60°C is designated as α-relaxation. This relaxation mode has already been observed in α-PVDF by either mechanical[21,22] or dielectric[23,24] dynamic analysis.

*Figure 5b* shows the TSCr spectrum obtained in XLPE. The torsional stress ($\sigma = 1$ MPa) was applied at $T_\sigma = 56$°C over 2 min. The spectrum obtained by thermostimulated creep consists of a very broad peak located at ~38°C. This peak has been assigned to the α relaxation mode frequently found in LDPE in the same temperature domain[25,26].

### *Relaxation/retardation map analysis*

TSCu and TSCr spectra are complex. The technique of fractional polarizations/stresses[5–8] allows us to resolve them experimentally into elementary spectra which can be analysed with the assumption that they are described by a unique relaxation/retardation time.

The technique of fractional stresses was applied to the resolution of the complex modes of these polymers. Results obtained in α-PVDF by TSCu are shown as an example in *Figure 6*. The narrow polarization window (5°C) was shifted by steps of 5°C between −5°C and 55°C. The envelope of the elementary peaks follows the same variations as the complex TSCu spectrum (*Figure 5a*). Above the α-mode, the magnitude of the elementary peaks cannot be dissociated from the baseline current. In contrast, for β-PVDF, the analysis was followed to higher temperatures.

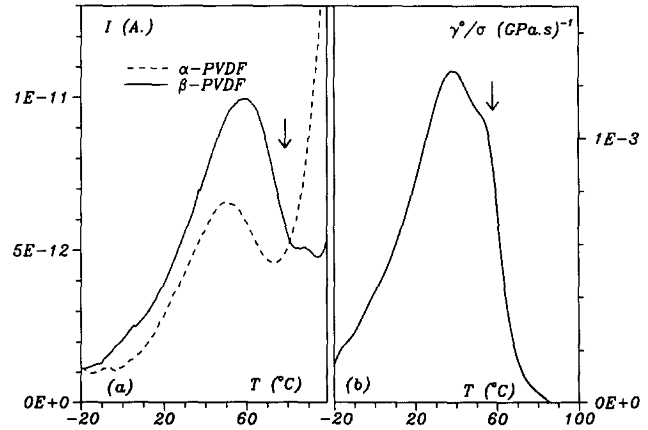

**Figure 5** (a) TSCu spectra of α- and β-PVDF in the α-relaxation mode temperature range. The arrow indicates the polarization temperature. (b) TSCr spectrum of XLPE in the α-relaxation mode temperature range. The arrow indicates the temperature of applied stress

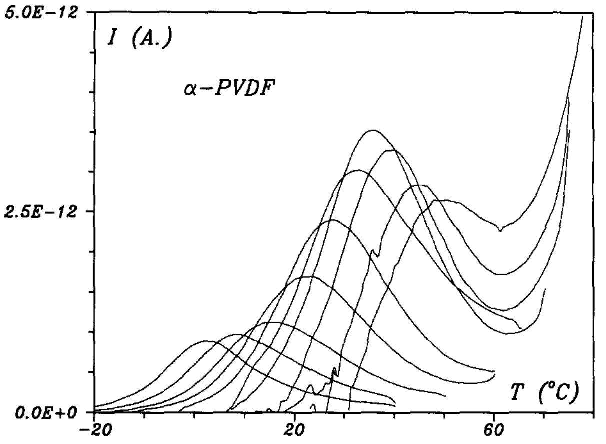

**Figure 6** TSCu elementary spectra of α-PVDF obtained by the technique of fractional polarizations

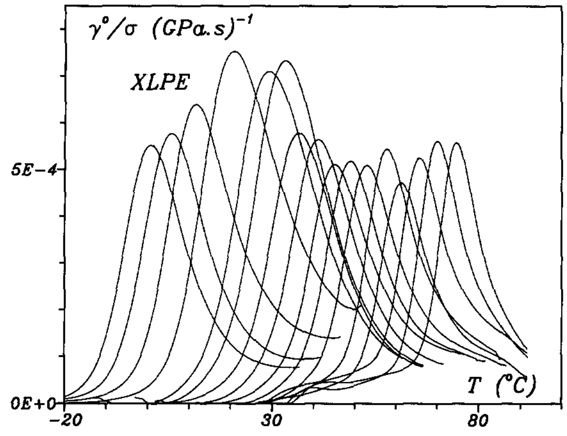

**Figure 7** TSCr elementary spectra of XLPE obtained by the technique of fractional stresses

The same method was applied for the resolution of the α-mode of XLPE by TSCr. The temperature window was the same as for PVDF. The set of elementary peaks obtained is shown in *Figure 7*. As in PVDF spectra, the envelope of the elementary peaks follows the variations of the complex TSCr spectrum (*Figure 5b*).

With the temperature window being narrow (5°C), each elementary peak is well described by a unique relaxation/retardation time $\tau$ ($T$). In TSCu, the relaxation time is defined by:

$$\tau(T)=\frac{P(T)}{j(T)} \tag{1}$$

where $j(T)$ is the current density at a temperature $T$, and $P(T)$ is the polarization. In TSCr, the retardation time is given by:

$$\tau(T)=\frac{\gamma(T)}{\mathrm{d}\gamma(T)/\mathrm{d}t} \tag{2}$$

where $\gamma$ is the strain.

*Figure 8* shows, on an Arrhenius diagram (semilogarithm diagram of $\tau$ *versus* reciprocal temperature), the distribution of relaxation times deduced from the analysis of the elementary peaks isolated in $\beta$-PVDF. Their linear relationship (each of them corresponding to the analysis of one elementary peak) shows that these relaxation times are described by an Arrhenius law:

$$\tau_i(T)=\tau_{0i}\exp\frac{\Delta H_i}{kT} \tag{3}$$

where $\tau_{0i}$ is the pre-exponential factor and $\Delta H_i$ is the apparent activation enthalpy.

The distribution of retardation times obtained from TSCr experiments on XLPE is shown in *Figure 9*.

For both polymers, relaxation/retardation times deduced from elementary peaks isolated above the α-relaxation mode intersect at a characteristic temperature designated as the compensation temperature $T_c$. At $T_c$, they have the same value $\tau_i(T_c)=\tau_c$, designated as the compensation time. So we can describe these relaxation/retardation times by using only one parameter, $\Delta H_i$:

$$\tau_i(T)=\tau_c\exp\left[\frac{\Delta H_i}{k}\left(\frac{1}{T}-\frac{1}{T_c}\right)\right] \tag{4}$$

The compensation temperatures are deduced from the semilogarithm diagram of pre-exponential factors *versus* activation enthalpies shown in *Figure 10*. For $\beta$-PVDF, $T_c=170$°C and for XLPE, $T_c=104$°C. Note that the compensation temperatures found for both polymers are close to their melting points: for PVDF and XLPE, $T_m=174$ and 105°C, respectively (*Figures 1* and *3*).

*Figure 11* shows the variation of the activation enthalpies as a function of the maximum temperature

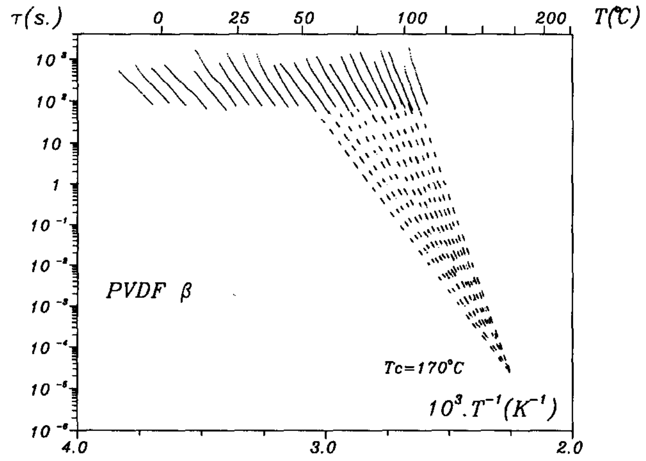

**Figure 8** Arrhenius diagram of relaxation times of $\beta$-PVDF

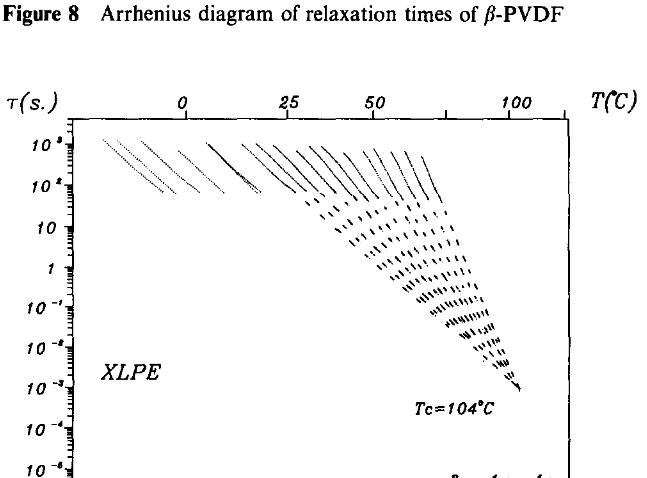

**Figure 9** Arrhenius diagram of retardation times of XLPE

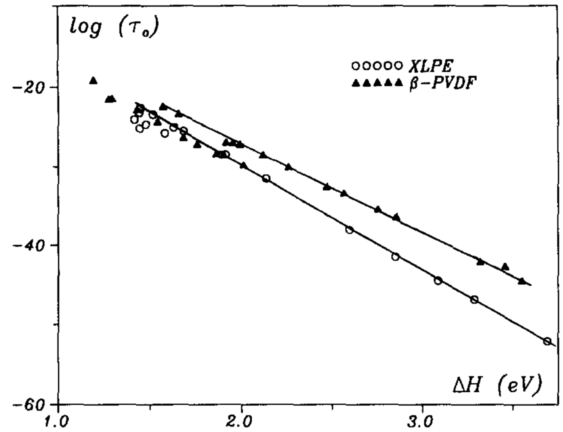

**Figure 10** Compensation diagram: pre-exponential factors *versus* activation enthalpies for XLPE and $\beta$-PVDF

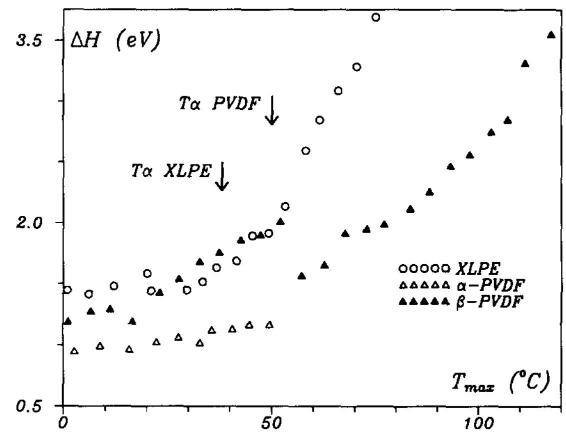

**Figure 11** Activation enthalpies *versus* maximum temperature of the elementary peaks for $\alpha$-PVDF, $\beta$-PVDF and XLPE. Arrows indicate the maximum temperature of the complex $\alpha$-mode

($T_{max}$) of the elementary peaks for $\alpha$-PVDF, $\beta$-PVDF and XLPE. For the $\alpha$-relaxation, the activation enthalpies remain rather constant. Above $T_\alpha$, a rapid increase of $\Delta H_i$ is observed: it is within this temperature domain that the compensation phenomena are observed (*Figures 8* and *9*).

## DISCUSSION

### $\alpha$-Process

For both polymers, the similar temperature position of the d.s.c. low temperature phenomenon and the $\alpha$-mode obtained with a low equivalent frequency should be noted. Thus, these two manifestations can be associated with the same molecular movements.

The low temperature thermal event described in this work has already been observed for PVDF in the $\alpha$-form[27–29]. It has been found to be sensitive to the thermal history of the material, e.g. room temperature annealing and fast quenching from the molten state favour its occurrence. It has been analysed as an endothermic phenomenon, a $C_p$ jump, or both. From our results, it appears that both processes occur. Several interpretations have been proposed, and these generally involve molecular motions relative to the crystalline regions.

Leonard *et al.*[29] have ascribed this phenomenon to an upper glass transition associated with the loop length in the folded chains of the lamellae. However, in this case, the lag between the two components of $T_g$ would be $\sim 100$°C, which seems rather large compared with values generally encountered in semicrystalline polymers ($\sim 30$–40°C[30]). Moreover, there is no clear reproducible $C_p$ jump as expected from a glass transition[27].

According to Loufakis and Wünderlich[27], this phenomenon would be associated with a condis glass transition in PVDF: conformational changes from *TGTG'* to *GTG'T* would be involved either inside the crystallites or at their surface. This kind of disorder is based on the conformational arrangement of the $\alpha$-phase. In this work, we have shown that this transition exists independently from the crystalline conformation ($\alpha/\beta$) of PVDF. These conformational movements would then occur at the surface of the lamellae. This would imply that an interface layer, with conformations differing from those inside the crystal, exists at the surface of the lamellae.

This suggestion is similar to that proposed by Mutter *et al.*[31] for crystalline polyethylene according to Raman studies. The resulting transition regions between the core crystal and the melt-like phase in semicrystalline polyethylene have been related to a conformationally ordered layer and to a disordered one. Both layers would be out of the crystal phase and would have different conformations to that of the coiled melt-like state. The presence of four different regions in the Raman spectra is not an indication of their relative position, but simply of their existence. Another possible interpretation of these results is the coexistence of two or three different conformations without the need for stacking.

Following the above interpretations, the low temperature endothermic event observed in the heating thermogram of XLPE could be explained by a lamellae surface melting phenomenon. Our d.s.c. results on XLPE show that a continuous partial melting at the surface of crystallites may exist because of the constant increase of the base line in the thermogram above the low temperature endothermic peak (*Figure 3*). In general, a lamellae surface melting phenomenon occurs continuously in a broad temperature domain. In contrast, the observed peak corresponds to a transition phenomenon localized in a narrow temperature range.

The relationship of this low temperature endothermic d.s.c. peak with the $\alpha$ mode could be explained by a particular mobility of the chains, for instance a possible solid-state chain diffusion. In this way, the perturbation of the crystal surface could be a consequence of this chain diffusion. Two- and three-dimensional exchange $^{13}$C n.m.r. experiments have shown the chain diffusion in polyethylene crystals below $T_m$[32,33]. This transport of crystalline chains corresponds to chain stem jumps in all-*trans* systems and to helical jumps in other semicrystalline polymers[32,33]. These kinds of movements could occur in all-*trans* XLPE and $\beta$-PVDF polymers and in the quasi-helical conformation of $\alpha$-PVDF. The endothermic manifestation of the $\alpha$-process is a different problem. The endothermic transition implies the disappearance of some order in the crystal structure. The combination of increased mobility in unordered regions—the $C_p$ jump—and a solid-state transition in the crystal core—the endothermic phenomenon—can be related to crystal chain segment diffusion and inherent surface adjusting. To date, this is the most classical interpretation of the $\alpha$-mode in polyethylenes and in highly crystalline polymers[34]. The increase of the interchain distance characteristic of the conformational evolution inside and at the surface of the crystal can explain the energetic evolution as described by Zerbi *et al.*[35] in the case of polymethylene chains.

From the models described above, the $\alpha$-process may be considered either as a crystallite surface mobility that is subsequently propagated into the crystal or as a surface reorganization resulting from movements of conformational defects in the crystallites. One of the characteristics of the d.s.c. results is that room temperature annealing is necessary to obtain the endothermic peak characterizing the $\alpha$-process. The ordering phenomenon that occurs upon room temperature annealing and gives rise to the endothermic peak may be located at the surface of the crystallites rather than in the crystal core since the mobility of the crystal is frozen-in at room temperature. Another important reason for this assignment is the observation of the $\alpha$-process independently from the crystalline phase of PVDF. Thus, the $\alpha$-process is attributed to an unfreezing of conformations at the crystallite surface. Once this mobility occurs it may propagate into the crystal. This hypothesis is discussed below.

### *High temperature compensation phenomenon*

Several observations have shown that between the $\alpha$-mode temperature ($T_\alpha$) and the $T_m$, crystallites undergo some evolutions which are: the solid-state thickening of polyethylene crystalline lamellae[4,36]; the ageing of piezo and pyroelectric activity of $\beta$-PVDF due to a lowering of the net polarization of crystallites[37]; and the shrinkage of oriented PVDF films[38]. All these changes can be related to conformational evolutions.

From relaxation/retardation map analysis, we have obtained a small variation of activation enthalpies in the $\alpha$-mode temperature range (*Figure 11*). In contrast, above $T_\alpha$, an important increase in the activation enthalpies occurs, resulting in the compensation phenomenon found in this high temperature domain. Such a compensation phenomenon is not observed for PVDF in the $\alpha$-form. Random copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) units have a ferro- to paraelectric (or Curie) transition below their melting point[10]. In this case, we have shown[39] that the compensation temperature corresponds to the transition temperature. For $\beta$-PVDF, evidence of a Curie transition has not yet been reported. By analogy with results obtained in P(VDF/TrFE) copolymers, the Curie transition of $\beta$-PVDF has been located around the melting point. This result is consistent with the divergence of the dielectric permittivity of PVDF below the fusion[40].

The Curie transition is of first order in P(VDF/TrFE) copolymers with high VDF content. Conformational disorder occurs at the phase transition, and the paraelectric phase (higher temperature one) consists of a random arrangement of *TT*, *TG* and *TG′* conformations which results in a pseudo-hexagonal packing in an expanded lattice[41]. Hence, this is an order/disorder solid–solid phase transition.

The monoclinic/hexagonal phase transition of hydroxyapatites is another example of crystalline material which for the compensation temperature, found by TSCu, corresponds to the transition temperature[42].

In the case of XLPE the existence of a high temperature compensation phenomenon may also be associated, as in the case of $\beta$-PVDF, with conformational evolutions in the crystalline phase. As in the case of $\beta$-PVDF, the crystal chain mobility associated with the compensation phenomenon of XLPE would correspond to an order/disorder solid phase transition. In this new phase the crystal chain would have a high degree of mobility.

The possibility of an intermediate phase in polyethylene has been recently introduced by Rastogi *et al.*[3]. This phase is the hexagonal one usually found in the chain extended morphologies of high pressure crystallized polyethylenes[43]. In the work of Rastogi, the hexagonal phase of polyethylene was described as a metastable transient phase that can exist in the temperature range of stability of the orthorhombic one. This hexagonal phase would correspond to a necessary condition for the lamellar thickening during the crystallization because of its high mobility.

We believe that the high temperature compensation phenomenon found in XLPE may correspond to the development of an hexagonal type phase. The important increase of chain mobility in this temperature range is a consequence of conformational changes. This intermediate phase must present an aperiodic structure, characteristic of hexagonal packing[44]. This aperiodicity may be provided by the thermally activated conformational disorder typical of the condis state[1]. The high temperature hexagonal phase of $\beta$-PVDF and XLPE cannot be experimentally observed, possibly because of the overlapping of the orthorhombic/hexagonal phase transition by melting. This behaviour has been discussed by Ungar[45] for the evolution from rotator phases in paraffins to hexagonal phases in polyethylenes.

It is known that phase formation is due to the minimization of the Gibbs free energy. The transition from the orthorhombic phase to the hexagonal phase is possible if, within a temperature range, the free energy of the hexagonal phase is lower than the free energies of both the orthorhombic phase and the melt. Conversely, if the melt becomes the most stable phase at a temperature below which the phase is orthorhombic, the hexagonal phase cannot exist.

There are several ways to reverse these possibilities. The introduction of disorder in the chains is a common one. Indeed, the hexagonal (paraelectric) phase of P(VDF-TrFE) copolymers is obtained by the addition of TrFE units in PVDF chains. Another example is the formation of the hexagonal phase of polyethylene by irradiation[43,45]. In both cases, structural disorder is introduced in the polymeric chains.

It is not only chemical treatments that produce a high temperature, high entropy solid phase. Entropy is a function of temperature, and in low crystallinity polymers (small stem length), an increase in the thermally activated disorder could be a mechanism for the 'frustrated solid–solid phase transition'. The high temperature compensation could correspond to the increase in concentration of conformational defects. This kind of mobility in the high temperature range of the solid state could be responsible not only for the phase transition but also for the physical changes occurring in semicrystalline polymers between the $\alpha$-mode and melting (see earlier).

Let us consider that the $\alpha$-mode corresponds to an unfreezing of conformations localized at the surface of the crystallites, i.e. the folds of lamellae. Below $T_\alpha$, the mobility associated with crystalline regions is frozen-in. A temperature increase through the transition manifests both by an endothermic peak and a $C_p$ jump due to the high disorder associated with the lamellae surface. This scheme for the lamellae surface is consistent with the condis description given elsewhere[1,27]. This would imply that the kind of order associated with these domains is reached, at room temperature, with slow kinetics. When the temperature is increased above $T_\alpha$, the mobility is propagated into the crystal. This mobility is responsible for the changes in the crystal structure, and therefore for the evolution of the physical properties of the polymers.

## CONCLUSIONS

A comparative study of crystal chain mobility in PVDF and XLPE has been performed by using d.s.c. and thermally stimulated techniques (TSCu and TSCr). D.s.c. studies have shown the presence of a conformational disorder in XLPE and in $\alpha$- and $\beta$-PVDF. The TSCu/TSCr studies have shown that there is a relationship between the endothermic d.s.c. phenomenon and the $\alpha$-mode of XLPE and $\alpha$- and $\beta$-PVDF. Both phenomena take place in the same temperature range.

By applying fractional polarizations/stresses to the resolution of the $\alpha$-relaxation/retardation mode in $\beta$-PVDF and XLPE, respectively, we were able to isolate a series of conformational movements responsible for an order–disorder phase transition. This phase transition could correspond to the formation of the paraelectric phase of $\beta$-PVDF and of the hexagonal phase in XLPE. This high temperature phase transition cannot be observed because of its overlap with the melting process.

The high temperature structure would result from the randomization of conformational defects in the crystal core. The disorder that characterizes the structure of the crystal is a consequence of the conformational evolution initiated at the surface of crystallites. The apparent order–disorder transition is close to the $T_m$. This behaviour can be explained by the similar values of the free energies for the isotropic melt and the conformationally disordered phase of these polymers.

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