Characterization of poled and non-poled β-PVDF films using thermal analysis techniques

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Abstract

β-poly(vinylidene fluoride)—β-PVDF—exhibits ferroelectric properties due to the special arrangement of the chain units in the crystalline phase. The ferroelectric phase can be optimised by poling the original stretched film, that tends to align the randomly organised crystallites against the applied field. In this work, polarised and non-polarised β-PVDF from the same batch are characterised by mechanical tests and a series of thermal analysis techniques, including DMA, TMA and DSC. The films exhibit mechanical anisotropy, and in the longitudinal direction the poled film presents larger mechanical properties, due to the higher structural organisation. Poled and non-poled show similar crystallinity levels but the melting temperature probed by DSC is higher for the non-poled film; for both films the melting peak exhibits a complex shape, indicating a heterogeneous crystalline organization. Two relaxation processes were found (β and α_c) by dynamic mechanical analysis (DMA). The β process, attributed to segmental motions in the amorphous phase, appears at the same temperature in both directions, but its intensity was found to be higher for the films tested in the longitudinal direction. For a given direction, the poled films exhibit lower peaks, due to the more organised amorphous structure. At higher temperature, the α_c-relaxation was related to the contraction of the films in the longitudinal direction during heating, recorded by thermal mechanical analysis (TMA). The onset of molecular mobility within the crystalline phase allows for cooperative diffusion processes in the amorphous phase, generating the randomisation of the initially oriented structure.
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1. Introduction

A wide range of studies have been reported in the last three decades on poly(vinylidene fluoride), PVDF, due to its attractive ferroelectric properties. PVDF is a semi-crystalline polymer, exhibiting different crystalline phases. The β-form is the one that provides the best ferroelectric properties, but the α-form is the more stable one. This phase is formed during simple crystallization upon cooling from the melt in quiescent conditions [1].

In order to prepare β-PVDF it is first necessary to prepare electrically inactive PVDF by a stretching process and then subject the sample to large and enduring electric fields. For the first step of the process, X-ray diffraction profiles

demonstrate that a complete conversion of all the α-PVDF crystallites into β-PVDF does not occur even at the highest stretch ratio (7:1). The second step, poling, is a process of re-alignment of the crystallite polarisations using static electric fields. Before poling has taken place the distribution of directions of polarisation of individual crystallites is random, whereas afterwards the polarisation directions have a biased distribution is space, and are biased toward the direction of the applied electric field. One of the models trying to explain the poling process involves rotation by 180° of each chain along its axis; other model involves also a rotation 60° [2].

Piezo- and pyroelecticity in β-PVDF results thus from alignment of dipoles by a static electric field and/or trapped charges injected during the poling process [3]. The β-PVDF structure is highly oriented; it has orthorhombic unit cells with a space group Cm2m (C_{2v}) with a planar zig–zag (all-*trans*) chain conformation and parallel CF$_2$ dipole moments of the adjacent chains parallel to the crystallographic

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b-axis. The conformation repeat unit has the electric moment of 7.0×10^{-30} Cm. β-PVDF has therefore a polarization of 131 mC/m^2 and exhibits the strongest electrical activity of all crystal modifications. The polymer has head-to-head (5%) and tail-to-tail (5%) defects that reduce the dipole moment of the planar zig–zag chain by 10%. The morphological organization of the ferroelectric polymer plays an important role in its thermo-mechanical properties. β-PVDF is composed by small crystallites with typical dimensions of ∼10 nm organised in groups of lamella, with partially oriented amorphous intralamella phase [4,5]. The density of the intralamella amorphous phase is higher than the density of the interlamella. In normal ferroelectrics (FE) the domain size should be larger that a critical value; otherwise, the domain will not be stable and collapse [6]. It was proposed that the amorphous phase in FE polymers plays an important role in the formation of stable ferroelectric domains, which should contain several crystallites and part of the amorphous phase. One or more lamella could participate of each domain. In fact, it has been concluded that the interphase between the crystalline and amorphous phases is of great importance for the polarization in β-PVDF [7]. In this interphase, a stress dependent orientation correlation of the molecular electric moments can exist, which in turn is induced by the complete orientation correlation of the moments in the crystalline phase. Estimations made by means of computer simulations shows that the thickness of the interface amounts to ∼1 nm [8] and that at usual supramolecular structure (crystallinity around 50%) the amorphous phase carries, by means of this interphase, an average polarization of 20 mC/m^2, i.e. around one third of the overall polarization. So, considering the rheological properties of the amorphous phase, the structure and dynamic of this phase will play an important role in the electro-mechanical properties of the material, too.

As the poling process will involve chains in the interphase as well as the rotation of the dipoles in the crystallites, strong changes in the thermal and mechanical properties of the material should appear due to the poling. The purpose of this work is to investigate how the poling process influences the thermo-mechanical properties of β-PVDF, paying special attention to the microscopic processes involved and especially to the influence of the amorphous phase. It will be proposed that thermal analysis techniques may give valuable informations on the difference between poled and non-poled PVDF. This study is among a broader project were other techniques are being used in order to relate structural/morphological behaviour of electro-active polymers with its piezoelectric and ferroelectric properties.

2. Experimental

β-PVDF films with 28 μm thickness were supplied by Measurements Specialities, Inc. (Fairfield, NJ, USA). Non-poled and poled (using a static electrical potential of several kV) films obtained from the same material were provided for this work. Therefore the only difference between the two films studied is the poling procedure applied on one of them.

Besides a series of thermal analysis used in the characterization of the β-PVDF films, quasi-static mechanical experiments were performed in a MINIMAT apparatus, from Polymer Laboratories, in the tensile mode at test velocity of d*l*/d*t* = 2 mm/min on ca. 4 cm × 1 cm rectangular samples in two different orthogonal directions. Due to the anisotropic features of the films originated by the processing method, experiments on both orthogonal directions were performed. The orientation along the direction of the extrusion of the original film will be labelled L (longitudinal), whereas the perpendicular orientation will be labelled T (transversal).

Differential scanning calorimetry (DSC) experiments were performed with a Perkin-Elmer DSC7 apparatus. The temperature of the equipment was calibrated with indium and lead standards and for the heat flow calibration only the same indium sample was used. All experiments (including the calibrations) were carried out on heating at 10 °C min^{-1}. The samples for the DSC studies were cut from the original films into small pieces and placed into 50 μl pans. An effort was made to keep the same sample weight for the different films (typically 4.153 ± 0.01 mg), in order to avoid differences in the thermal resistance of the system.

Dynamic mechanical analysis (DMA) and thermal mechanical analysis (TMA) were carried out in a Perkin-Elmer DMA7e apparatus in heating mode at 2 °C/min, using the tensile mode. In all cases, rectangular samples were cut from the original sheets, with ca. 2 mm width and 10 mm distance between clamps. For the DMA experiments, a static stress of 6.00 MPa was applied over a dynamic stress of 3.00 MPa of amplitude, that allowed to maintain the sample tough. DMA experiments were performed in the temperature range from −50 to 120 °C, whereas in TMA temperature varied from 30 to 140 °C. In the TMA experiments a small force of 10 mN was applied to the sample in order to keep it vertical during heating.

3. Results and discussion

3.1. Quasi-static mechanical experiments

The determination of the mechanical properties are among the most important characterization procedures to be performed in polymer systems, as it will determine the possibility of using the material for certain applications. Moreover, differences detected in different samples may reflect morphological variations occurring due to physical changes on a system induced by the processing of the material. This is the case of the effect of stretching and poling during the processing of the β-PVDF films studied in this work. Fig. 1 shows representative stress–strain data obtained in both T (Fig. 1a) and L (Fig. 1b) directions. As already reported [9], a
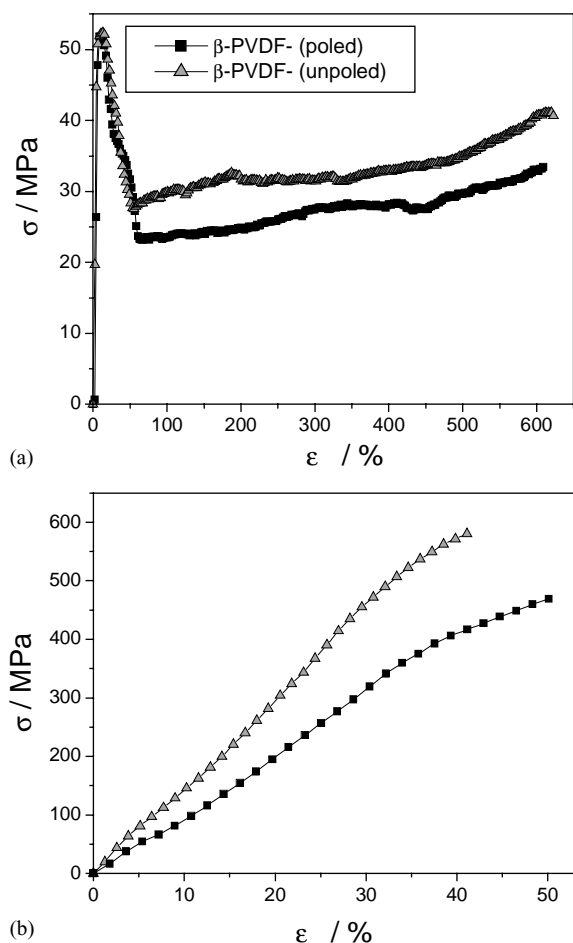
Fig. 1. Tensile stress–strain results obtained along the T direction of the β-PVDF films (a) and along the L direction (b) with respect of the extrusion direction (T) on the poled (squares) and non-poled (triangles) films. The experiments were performed at room temperature at $dl/dt = 2$ mm/min.

strong anisotropic behaviour is found, originated by the processing route employed in the preparation of the films. From the results in Fig. 1, it can be concluded that the mechanical properties along the T direction are similar in both films. In fact, no significant differences are detected in the two films, that have similar modulus (secant modulus at 5% of 1.1 ± 0.1 GPa), and ultimate stress (36 ± 8 MPa) and strain (615 ± 10). In the L direction the behaviour is much less ductile than in the T direction, and not apparent yield is found. Significant differences are found in this direction: for the poled and non-poled films the secant moduli at 5% are 1.5 ± 0.1 and 1.2 ± 0.1 GPa, respectively; the stresses at break are 580 ± 20 and 468 ± 20 MPa and the ultimate stresses are 42 ± 5 and 50 ± 5 MPa, for the poled and non-poled films, respectively. It can be conclude that the poling procedures enhanced the mechanical properties of the films, especially their strength. A possible reason for this behaviour can be the different conformation in the interfaces between the crystallites existing between poled and non-poled films. Though such regions are formed by amorphous regions in both cases,

a preferential orientation in the interphase region between the crystalline and the non-crystalline phases and in the amorphous part itself must exist for the poled samples. The less organized structure existing in the non-poled samples should have inferior mechanical performance, which are reflected in our results. It is interesting to note that such morphological differences are reflected in the properties along the L direction, and apparently no consequences are detected along the T direction, that exhibit intrinsically a very ductile behaviour.

3.2. Differential scanning calorimetry

With the main goal of comparing the effect of the poling on the β-PVDF films, only the first DSC runs of the poled and non-poled films are reported in this work. Fig. 2 shows the typical traces for poled and non-poled samples. The DSC scans present significant differences in the positions of the melting peaks: the onset temperatures are 156.3 °C for the poled and 160.1 °C for the non-poled films. Several factors can have influence on the change of the melting temperature.

Morphologically, a decrease in T_m may be due to a thinner lamellar population. However, this possibility seems to be improbable, as it should be expected that the poling procedure should not diminish the quality of the crystalline phase. An argument for that is that the enthalpy of the melting, calculated from the area of the peaks, is very similar for the two films: 46 and 49 J g^{-1} for the poled and non-poled samples, respectively. Considering a melting enthalpy for a fully crystallised PVDF of 104.5 J g^{-1} [10], such values indicates that the degree of crystallinity of the studied films is similar and around 46%, which is consistent with previous results [9].

Another possibility for the differences in T_m could be the differences in the crystalline organisation, that may be also linked to the relative amount of the α and β structures. In
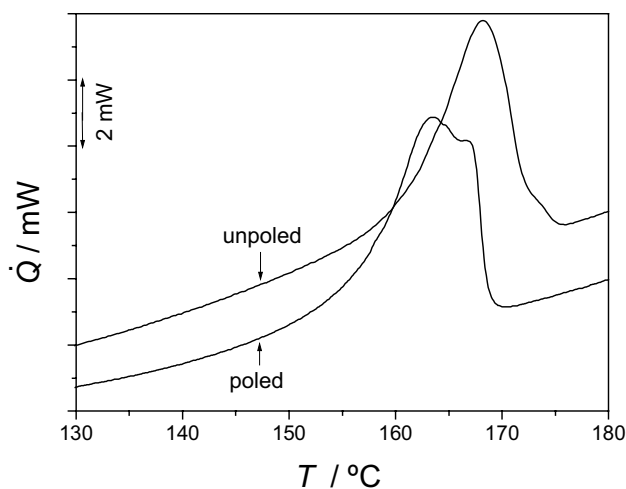

Fig. 2. DSC traces for the poled and non-poled β-PVDF films, performed at 10 °C min^{-1} (first runs).

fact, it was demonstrated before with FTIR data that poling films have higher relative contents of β-crystals, in comparison with α ones [11]. For the poled sample we have a more oriented structure where the dipolar moments are directed towards a preferential direction. In the non-poled films, on the other hand, many oriented nanometric regions will exist, with random orientation among them and thus, with sudden changes in orientation near the interphases. Therefore, from a thermodynamic point of view, the crystalline structure of the poled film should present less entropy than the non-poled film. As the melting structure is similar for both situations, we expect that the poled film should have higher melting entropy (ΔS_m) than that of the non-poled film. Considering that at the phase equilibrium we have $T_m = \Delta H_m / \Delta S_m$, it should be detected a lower melting temperature for the poled film, as it was observed experimentally (Fig. 2). Again, the similarity in the area of the peaks observed for the two samples suggests that the differences in T_m should not be due to enthalpic reasons (i.e. ΔH_m is similar for both films).

Note that the melting peak of the poled peak shows a high temperature shoulder at ca. 167 °C. Also in the non-poled a low-intense endothermic process appears at higher temperatures. Other experiments performed at the same and other heating rates confirmed that the melting peak of both films is complex. Again, this may reflect the presence of different crystalline organizations, including the co-existence of the α and β phases.

3.3. Dynamic mechanical analysis

The effect on poling may have influence on the chain dynamics within the PVDF structure. A suitable method to monitor molecular mobility and the macroscopic viscoelastic behaviour in polymers is by employing DMA. Fig. 3 shows the temperature dependence of the storage modulus (E') and the loss factor ($\tan \delta = E''/E'$), at 1 Hz, of the poled

and non-poled films. Each film was analysed in both principal directions (L and T).

Two main relaxations are detected in all experiments, in agreement with previous DMA results [12]. In the low temperature region, a process is found with a maximum in $\tan \delta$ at ca. −30 °C, assigned to the segmental motions of the amorphous regions [13,14], usually labelled β or α_a. Previous dielectric relaxation spectroscopy studies on the same film indicated that the central relaxation time of this process depends upon temperature according to the Vogel–Tammann–Fulcher equation [15], as it is observed in the cooperative relaxations assigned to the dynamic glass transition in amorphous and other semi-crystalline polymers.

The $\tan \delta$ peak of the β process seems to be more intense for the longitudinal sample, in both poled and non-poled films. A similar behaviour was observed, for example, for the same process in polyethylene (PE) [16], indicating that the viscoelastic properties in anisotropic specimens depend strongly on the direction of the test [17,18].

When comparing the effect of poling, the results suggest that, for the same test-direction, the $\tan \delta$ peaks of the non-poled films have higher intensity than the corresponding peak for the poled film. This can be ascribed to the less restricted mobility in non-poled samples that, despite affecting the amplitude of the relaxation, does not influence its dynamics (the position of the peaks in the temperature axis is very similar). In non-poled samples, the chains in the amorphous samples are relatively free to rotate, helping neighbour crystallites to compensate the polarization effects and minimizing the overall energy of the sample. The effect is related to the compensating charges piled up at the crystalline phase of the semicrystalline polymer. After poling, the movement of such chains are somewhat frozen, reducing the intensity of the cooperative motions within the amorphous phase. We may have also an influence of the interphase between crystallites in the non-poled film, that may
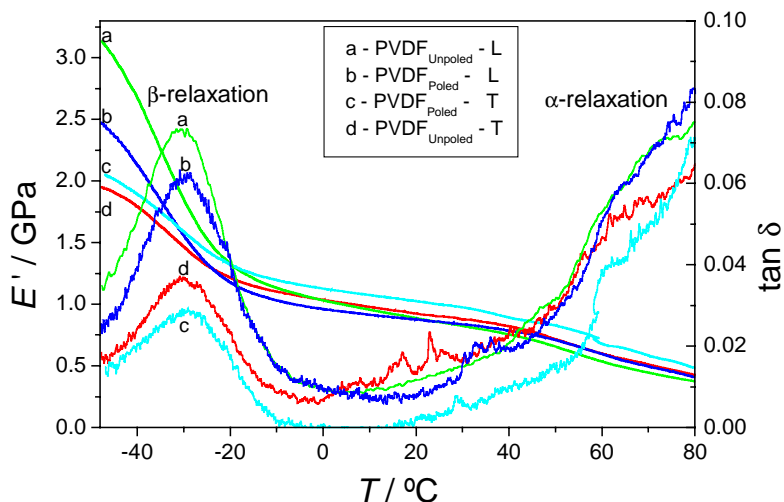

Fig. 3. DMA spectra (storage modulus and loss factor) for the poled (b and c) and non-poled (a and d) β-PVDF films, analysed in both L (a and b) and T (c and d) directions. The experiments were carried out at 2 °C min⁻¹ and at a frequency of 1 Hz.

also contribute to an extra macroscopic dissipation of mechanical energy, increasing tan δ.

Above 30 °C a new relaxation emerges (Fig. 3) that, in contrast with the β-relaxation, is badly defined in a tan δ plot. This process, labelled α or α_c, is associated with motions within the crystalline fraction, previously detected by DSC (Fig. 2) [13,14,19]. This process is also found in a variety of flexible semicrystalline polymer, including polyethylene, poly(methylene oxide), poly(ethylene oxide) and isotactic polypropylene [20,21] and its origin should be similar to the one observed in PVDF. From the obtained results (Fig. 3), it is difficult to correlate the features of this process with the direction and the poling effect. In a previous study, it seemed that the non-poled films exhibit more intense damping properties in the region of the α_c-relaxation when tested in the L-direction [11]. However, the present results are not able to confirm such findings.

At low temperatures, higher values of the storage modulus are found for the samples tested along the L-direction, as the molecular orientation is higher. However, no significant differences exist in the storage modulus in all films above the occurrence of the β-relaxation. It seems that the decrease of stiffness taking place during the dynamic glass transition will overcome the effects of the orientation due to poling and so, the differences in orientation are not reflected in the storage modulus around room temperature. In this context it should be noticed that the values of E' are of the same magnitude as the modulus found in the quasi-static mechanical experiments.

3.4. Thermal mechanical analysis

The changes in the geometry of the films upon heating were monitored as a function of temperature (Fig. 4). The experiments in both L and T directions allowed recording the variations in the length of the films along the two principal directions during heating. Strong variations in the length of the samples are measured along the L direction above ca. 70 °C, due to the release of the orientation induced during the stretching of the film by the processing of β-PVDF (polarized and non-polarized). This contraction upon heating is very common in retractable films used in packaging, usually produced in polyethylene. Transversally to the induced orientation, no significant changes are found in both poled and non-poled films. In fact, only a small increase in this dimension is detected, that reflects the shrinking in the longitudinal direction (pushing apart the chains that are initially oriented preferentially along the L direction) and also the own dilatation of the film. The TMA results have interest from a practical point of view, giving in the temperature axis the dimensional stability of such kind of films and the recovery extent of their geometry, that may be useful for certain applications.

Surprisingly, the discussion about the molecular origin of the geometrical recovery in oriented films of semicrystalline polymers during heating is very scarce. Note that
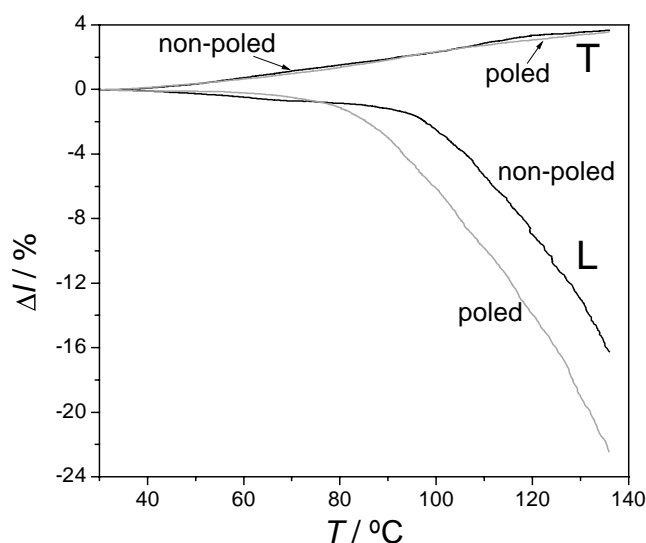

Fig. 4. TMA traces, showing the variation in the distance between clamps (Δl) with temperature, relatively to the initial length, in samples subjected to a small load (10 mN). Temperature rate: 2 °C min^{-1}. Poled and non-poled samples were measured, in the T and L directions.

this should not be related with a simple onset of mobility within the amorphous phase near T_g as found in amorphous systems, because the glass transition of PVDF is located at much lower temperature (β-relaxation in Fig. 3). The changes in the dimensions along the L direction could not be also attributed to the melting of the crystalline structure, either (that could induce the instantaneous randomisation of the orientated structure), as the melting occurs well above the onset of the recovery process (see melting process in Fig. 2).

In this work it is proposed that the origin of the contraction onset of oriented PVDF films could be related with the α_c-relaxation, which was detected by DMA (Fig. 3). This process induces some mobility within the chains that may initiate the loosing of molecular orientation. Thus, a deeper inspection on the mechanism of this relaxation should be reviewed here. As for polyethylene, the α_c-relaxation process in PVDF should also involve 180° flip motions of the chain stems within the crystalline lamellae [20–22]. In polyethylene, this screw motion process involves both a translation and a rotation of one –CH$_2$– unit, such that the portion of the chain in the crystallites is in its energetically most favourable position in the lattice before and after the jump [23]. A similar mechanism, also involving the –CF$_2$– groups should also occur in PVDF. A significant cooperative character was found for polyethylene, indicating that diffusion processes involving chains in the amorphous region should accompany the α_c-relaxation [24] (such cooperativity was also found in PVDF [25]). This findings are consistent with the fact that this process emerges mechanically from an additional shear of the amorphous regions that needs to occur in order to provide the chain transport through the lamellae [20,21]. Concluding, a significant mobility arises in both the

crystalline and amorphous regions in PVDF with the occurrence of the α_c-relaxation. During heating, the starting of this process induces cooperative diffusion mobility within the chains that tends preferentially to give rise to a more random amorphous structure due to entropic reasons. Note that below the temperature of the α_c-process (very high relaxation times) the amorphous regions are kept tight between the crystalline lamellae, having significant mobility above T_g (yet limited by the crystalline fraction) but exhibiting preferential orientation.

The results in Fig. 4 point out for an earlier contraction of the sample in the L direction for the poled sample, when compared with the non-poled sample. The DMA results did not show a α_c-relaxation at lower temperatures or more intense for the poled film, in order to be consistent with the connexion of this relaxation and the contraction process. Therefore, more work is needed, including comparative studies with other polymeric system, in order to confirm the hypothesis proposed in this study.

4. Concluding remarks

A series of thermal analysis techniques were used in an integrated way (the main conclusions were obtained by combining the results from different tests) in order to characterise β-PVDF films, subjected or not, to a previous poling process that improves the piezoelectric characteristics of the material. It was found that thermal analysis is a suitable way to understand differences in the morphological and structural point of view induced by poling. From the results obtained in this study we can draw the following conclusions.

- Quasi-static mechanical results pointed out for a highly anisotropy in all β-PVDF films. Along the T direction both poled and non-poled films present a similar ductile behaviour, whereas in the L direction the poled film exhibits superior mechanical properties.
- Only the melting peak is observed by DSC, with similar enthalpies for poled and non-poled films (corresponding to ca. 46% crystallinity).
- The melting temperature of the poled films is lower than for the non-poled ones. This fact was ascribed to the lower entropy existing in the poled film (increasing ΔS_m). The shape of the melting peak for the two films is complex, revealing the co-existence of different crystalline organizations.
- Dynamic mechanical analysis detected both β (attributed to the dynamic glass transition) and α_c (assigned to motions within the crystalline structure) relaxations. For all samples and orientations the β relaxation appears at the same position (ca. $-30\,^{\circ}C$ at 1 Hz). However the intensity of the tan δ peak is found to be higher for the films aligned in the L direction, indicating that the damping properties are higher along the molecular orientation than

transversally to it. The results point out for higher damping capability of the non-poled material, relatively to the film subjected to poling. This may be attributed to the extra-dissipation of mechanical energy within the interphase between the crystalline and the amorphous phase in the non-poled sample, or to the less organised structure in these regions and in the amorphous part of the material itself. The α_c-relaxation may have important implications in the practical use of such films as it will determine the viscoelastic properties at room temperature. No significant differences are found in this process when comparing the different films and orientations.

- Thermal mechanical analysis allows to conclude that above $70\,^{\circ}C$ the length along the L direction continuously decreases down to values that can reach more than 20% reduction. The same is not observed in the T direction. The shrinkage of the film could be a result of the occurrence of the α_c-relaxation. Indeed, the onset of molecular mobility within the crystalline, assigned to this relaxation, allows for cooperative diffusion processes in the amorphous phase, generating the randomisation of the initially oriented structure, which is highly favourable from a entropic point of view.

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