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Poling of β -poly(vinylidene fluoride): dielectric and IR spectroscopy studies

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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 piezoelectric properties of the material can be optimised by poling the original stretched film. The main effect of the poling process is the alignment of the randomly organised dipolar moments against the applied field. In this work, poled and non-poled β -PVDF from the same batch are characterised by dielectric spectroscopy. The origin of the electrical and mechanical response of poled and non-poled β -PVDF were further explored by far IR spectroscopy and discussed on a molecular level. The main effect of the poling process on the dielectric response of the material is a small increase of the dielectric constant due to the preferential alignment of the main dipolar contribution and a slight decrease of the dielectric loss, due to the more organized amorphous structure. The conductivity is strongly increased by poling, especially the high-temperature conductivity, ascribed mainly to hopping conductivity due to free charges induced during poling. FTIR experiments indicate that the origin of these effects and also of the variations in the thermo-mechanical response of the material can be found in the reorientation of the crystalline dipoles along the poling field, together with a partial reduction of the amount of α phase and an increase of the amount of β phase. The α to β transformation, mainly due to the stretching process, seems to be optimized by the poling process.

1. Introduction

Ferroelectric polymers are of great scientific and technological interest. The rapid commercialization of piezoelectric transducers made from these materials also represents a model for technology transfer. Ferroelectric polymers are a rich system for the study of phase transitions, relaxational processes and ferroelectricity; they

exhibit all the interesting physical phenomena associated with inorganic ferroelectrics and yet exhibit fundamentally different microscopic interactions, dominated by hydrogen bonding and van der Waals forces [1-3].

Poly(vinylidene fluoride) (PVDF) is the prototypical ferroelectric polymer. A wide range of studies has been reported in the last three decades on PVDF and its copolymers, 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 [1-3].

PVDF is a linear fluorinated hydrocarbon with a repeat unit ($\text{CH}_2\text{-CF}_2$) of spacing 2.6 Å. The PVDF chains have a net dipole moment, pointing from the electronegative fluorine to the electropositive hydrogen, producing a net dipole moment nearly perpendicular to the polymer chain. These chains can crystallize in a quasi-hexagonal close-packed β phase structure with dipoles of all chains aligned in a structure with maximum polarization $P \approx 0.13 \text{ C/m}^2$. Poling and switching are accomplished by applying a large electric field perpendicular to the chains to reverse the direction of polarization [3].

In order to prepare β -PVDF it is first necessary to prepare electrically inactive α -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 realignment 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 in space, and are biased towards the direction of the applied electric field. One of the models aiming to explain the poling process involves rotation by 180° of each chain along its axis; another model involves also a rotation by 60° [4].

This polarization is based on the cooperative orientation of the monomer dipoles ($\text{CH}_2\text{-CF}_2$) in ferroelectric domains [5]. The β -PVDF structure is highly oriented; it has orthorhombic unit cells with a space group $\text{Cm}2\text{m}$ (C_{2v}) with a planar zigzag (all-*trans*) chain conformation and parallel CF_2 dipole moments of the adjacent chains parallel to the crystallographic b -axis. The conformational repeating unit has an electric moment of $7.0 \cdot 10^{-30} \text{ Cm}$. 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 zigzag chain by 10%.

In PVDF the melting temperature ranges from 160 to 180°C , being lower than the expected Curie temperature T_C calculated in the range 205 to 208°C by extrapolation of the intersect of the inverse of the dielectric permittivity with the temperature axis and the temperature behaviour of the hysteresis loops [3]. So, heating the poled β -PVDF films to temperatures lower than the melting temperature induces important conformational changes, but not a complete phase transition and thus not a complete depolarization of the polymer [3].

The ferro-, piezo-, and pyroelectric properties of PVDF are exploited in a number of applications such as sensors of heat, pressure and sound, in which the material may be subjected to severe temperature changes or mechanical stresses [2,3]. An important issue is the dependence of those properties on the structure of this polymer. β -PVDF is composed of small crystallites with typical dimensions of $\approx 10 \text{ nm}$ organised

in groups of lamellae, with partially oriented amorphous intralamellar phase [3,6]. In normal ferroelectrics (FE) the domain size should be larger than a critical value; otherwise, the domain will not be stable and collapse [7]. 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 lamellae could participate of each domain. In fact, it has been concluded that the interface between crystalline and amorphous phases is of great importance for the polarization in β -PVDF [8]. At this interface, 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 show that the thickness of the interface amounts to ≈ 1 nm [8] and that at a usual supramolecular structure (crystallinity around 50%) the amorphous phase carries, by means of this interface, an average polarization of 20 mC/m^2 , i.e., around one third of the overall polarization [8]. So, considering the rheological properties of the amorphous phase, the structure and dynamics of this phase will play an important role in the electro-mechanical properties of the material, too.

As the poling process will involve chains at the interface as well as the rotation of the dipoles in the crystallites [4], significant 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 dielectric properties of β -PVDF, paying special attention to the microscopic processes involved and especially to the influence of the amorphous phase. Furthermore, far IR spectroscopy has been also carried out in poled and non-poled samples in order to evaluate such effects on the molecular level.

2. Experimental part

The starting material was a $28 \mu\text{m}$ thick commercial β -PVDF film from Measurements Specialties, Inc. (Fairfield, NJ, USA). Non-poled and poled (using a static electrical potential of several kV) films obtained from the same batch were provided by that company for our work. Therefore, the only difference between the two films studied is the poling procedure applied on one of them.

Measurements of the dielectric constant were performed in a home-built cryostat and a Lock-in amplifier (Stanford Research model SR850) was used to measure the in-phase and out-of-phase currents in the sample. The applied signal for eight frequencies in the range 100 Hz to 100 kHz was 1 V. Using a standard calibration procedure the measured signals were converted into values of ϵ' and $\tan \delta$. The samples, metallised and plain, were cut into small square pieces of approximate dimension 7 mm by 7 mm and on the plain samples the electrodes were made by painting a circular region of about 5 mm diameter and thin copper wires attached with a conducting paint; the metallised samples did not need painting. The temperature was varied between -190 and 150°C and was maintained stable within 0.2°C during a frequency run. The error of measurements of signals is less than 1% and, therefore, the only significant error in the values of ϵ' and $\tan \delta$ is due to the error in the measurements of sample area and thickness.

Infrared spectra were obtained in transmission mode on a Bruker 66V spectrometer from 400 to 6000 cm^{-1} using polarised light in perpendicular (\perp) and parallel (\parallel) modes, with a resolution of 1 cm^{-1} . Here, perpendicular and parallel refers to the

orientation of the polarization of the light with respect to the preferred chain orientation (draw direction).

3. Dielectric spectroscopy

The determination of the dielectric constant and its variation with temperature and frequency is among the most important characterization procedures to be performed in polymer systems, especially when the material can be used for applications involving its pyro- and piezoelectric properties. Moreover, differences detected in different samples may reflect morphological variations occurring due to physical changes induced by the processing of the material. This is the case of the effect of poling during the processing of β -PVDF films studied in this work.

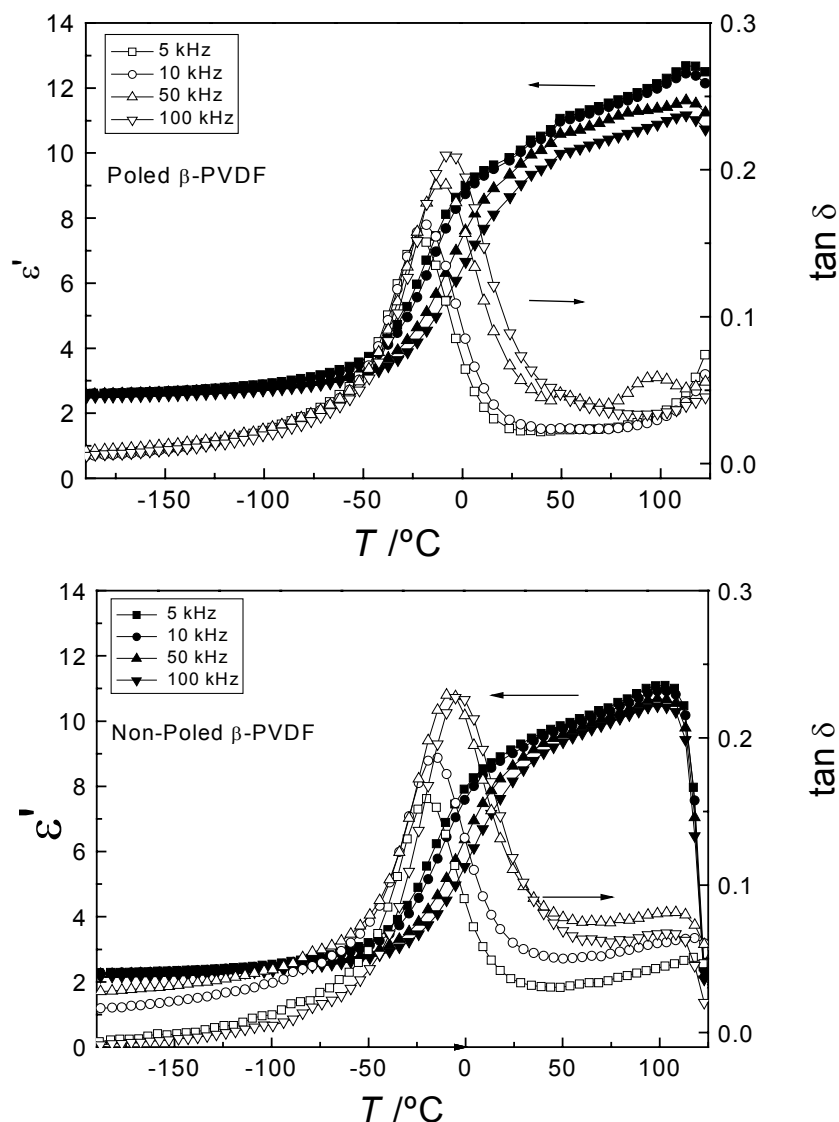


Fig. 1. ϵ' and $\tan \delta$ vs. temperature for poled (above) and non-poled (below) β -PVDF films measured at several frequencies between 500 Hz and 100 kHz

Measurements of the complex dielectric constant were performed in poled and non-poled samples in order to evaluate the effect of polarization alignment both on the overall response of the dielectric permittivity with temperature and frequency and, in

particular, on the different relaxations observed in this material. The results obtained for poled [9] and non-poled samples (Fig. 1) reveal the low-temperature β relaxation, assigned to the glass transition dynamics. Therefore, this process is mainly probing the cooperative segmental motions within the amorphous phase. The α_c relaxation of β -PVDF is proposed to show up around 100°C [3]. This relaxation is associated with molecular motions within the crystalline fraction of the material. Instead of a clear account of the α_c relaxation, in this temperature range a decrease of the dielectric constant, which is smoother for the poled sample, is observed. The maximum of the dielectric constant begins at $\approx 116^\circ\text{C}$ in the poled sample [10,11] and at $\approx 105^\circ\text{C}$ for the non-poled one.

The slope of the decrease of the dielectric constant with increasing temperature in the non-poled samples slightly varied in successive heating runs, but being always larger than the decrease observed for the poled samples. In this temperature region a shrinking of the sample has been measured that accounts, at least in part, for the decrease of the dielectric constant [10]. Further, an increase of $\tan \delta$ also occurs in this temperature region. The increase of $\tan \delta$ is due to an increase of the conductivity of the material, and has been discussed in refs. [10,11]. The geometrical effect and especially the high-temperature conductivity mask the detection and study of the α_c relaxation by dielectric spectroscopy. So, no obvious dipole loss process was detected above 50°C. Nevertheless, the existence of the α_c relaxation in that region has been proven by means of mechanical measurements [10].

When an electric field is applied to the sample, the structural changes are reflected in the behaviour of the dielectric permittivity, both with temperature and frequency. The values of various relevant dielectric parameters for the two samples are summarized in Tab. 1 and Tab. 2. Both poled and un-poled samples show the same main features of the dielectric behaviour, though important changes occur in the overall values of ϵ' and $\tan \delta$.

Tab. 1. Relevant dielectric parameters for poled and non-poled β -PVDF samples, related with the β relaxation. The values are given for a frequency of 10 kHz

	ϵ' (25°C)	$\Delta\epsilon'_\beta$	$\tan \delta_{\max}$	$T(\tan \delta_{\max}) / ^\circ\text{C}$
Non-poled	8.7	5.9	0.23	-6.5
Poled	9.5	5.9	0.15	-18.7

Tab. 2. Vogel-Tammann-Fulcher and fragility parameters for the β relaxation of poled (P) and non-poled (NP) β -PVDF

	τ_0 / s	$E_{\text{VTF}} / \text{eV}$	T_0 / K	m
Non-poled	$0.3 \cdot 10^{-11}$	0.061	201.5	99
Poled	$0.5 \cdot 10^{-11}$	0.062	196.5	92

The permittivity of the poled sample is slightly higher than the non-poled one, in the whole temperature range studied. For example, the value of ϵ' at 25°C (i.e., above the β relaxation) is 8.7 for the non-poled sample to 9.5 for the poled one (Tab. 1). The decrease in ϵ' with decreasing temperature due to the β relaxation was analysed

by considering the difference of ϵ' before ($T = 25^\circ\text{C}$) and after ($T = -75^\circ\text{C}$) the β relaxation, $\Delta\epsilon'_\beta$. The decrease in the dielectric constant due to the β relaxation is the same in both poled and non-poled β -PVDF. As the β relaxation is ascribed to the glass transition dynamics occurring in the amorphous regions [12,13], this observation is consistent with the fact that the poling process does not affect in a significant way the dipole orientation in the amorphous part of the semicrystalline polymer.

The value of the maximum $\tan \delta(T)$ of the β relaxation is similar for both films, but the temperature of the peak suffers a decrease with poling (see Tab. 1). This observation means that the glass transition temperature of the poled material is lower than of the non-poled one, indicating that for the former the amorphous chains are less constrained.

The dynamics of β relaxation was analyzed by the Vogel-Tammann-Fulcher relaxation formalism (Fig. 2)

$$\tau = \tau_0 \exp(E_{\text{VTF}}/k(T - T_0)) \quad (1)$$

where E_{VTF} is the VTF energy, k is the Boltzmann constant and T_0 is the critical temperature at which molecular motions in the material become infinitely slow. The fittings are presented in Fig. 2 and the parameters obtained for the different samples are summarized in Tab. 2.

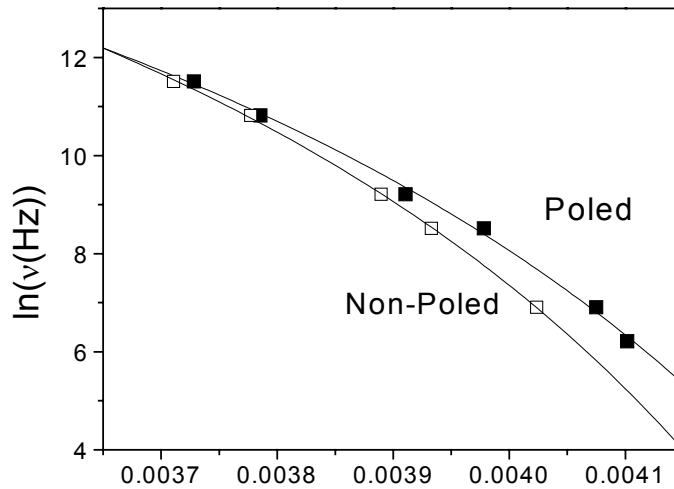


Fig. 2. Vogel-Tammann-Fulcher fits of the β relaxation of poled and non-poled β -PVDF films (right)

The poling process does not affect the characteristic parameters of β relaxation. Similar values for the activation energy are obtained. On the other hand, the Vogel-Tammann-Fulcher temperature is larger and the cut-off time shorter for the non-poled sample. The difference in T_0 is intimately related to the higher T_g of the non-poled sample.

A consequence of the values of the fitting parameters of the VTF relaxation plot is the calculation of the fragility parameter [9]:

$$m = \frac{E_{\text{VTF}}/kT_g}{(\ln 10)(1 - T_0/T_g)^2} \quad (2)$$

where m is an indication of the steepness of the variation of the material properties (viscosity, relaxation time, ...) as T_g is reached. A high m value defines a fragile material whereas a strong material will be characterized by small m values.

The values of several glass-forming amorphous polymers range from 46 (polyisobutylene) to 191 (poly(vinyl chloride)) [14]. The $m(T_g)$ value calculated with the VTF parameters is determined at the glass transition temperature (T_g) where the relaxation time is equal to 100 s. The fragility parameters of poled and non-poled β -PVDF are very similar. This demonstrates that only the amorphous part of the material is involved in this relaxation process and that poling does not affect in a significant way the amorphous part.

The main difference between the non-poled and the poled samples occurs in the region of α_c relaxation. As already discussed before, two effects are superimposed to the expected relaxation [3] in this temperature region: a geometrical effect due to the shrinkage of the sample and an increase of the conductivity of the sample [10].

In the poled sample, an increase in $\tan \delta(T)$ starting at $T \approx 65^\circ\text{C}$ and an anomalous decrease of $\varepsilon'(T)$ at $\approx 90^\circ\text{C}$ is observed (Fig. 1). On the other hand, the non-poled samples show a sudden decrease of the dielectric constant $\varepsilon'(T)$. Repeated temperature runs in both samples indicated that the slope of the decrease of the dielectric permittivity with temperature varied, especially in the non-poled samples. On the other hand, this decrease is always more pronounced in the non-poled than in the poled samples.

At $T \geq 70^\circ\text{C}$ the frequency dependence of the real and imaginary parts of complex permittivity of β -PVDF can be fitted by Eq. (3) [10,11]:

$$\varepsilon^*(\nu) = \varepsilon_\infty + B \operatorname{Im}(2\pi i \nu)^a \quad (3)$$

where ε_∞ is the high-frequency limit of the real part of dielectric permittivity, which corresponds to the static permittivity of the nonconductive crystal, B and a are constants. The obtained values ($0.10 < a < 0.25$) are typical of hopping conduction in disordered media [15].

The fact that the high-temperature conductivity exists in both poled and non-poled samples (Fig. 3) and behaves in a similar way, but that the values are larger for the poled samples, indicates that some charges could be ionic species from chemical additives used for polymerization as well as water dissociated into the polymer, but that charges must be also induced during the poling of the material [3]. The configurational changes accompanying the poling process do not seem to influence the conduction mechanisms, but the number of charge carriers and/or their mobility.

It can be concluded that the poling procedures enhanced the dielectric properties, besides improving the mechanical properties of the films [16]. A possible reason for this behaviour can be the different conformation at 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 interface region between the crystalline and the non-crystalline phases and in the amorphous part itself must exist for the poled samples. Poling induces differences in the crystalline organisation: 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 interfaces. This is in agreement with previous DSC results in which a decrease of

the melting temperature upon poling has been observed, with no changes in the degree of crystallinity of the material ($\approx 46\%$) [16].

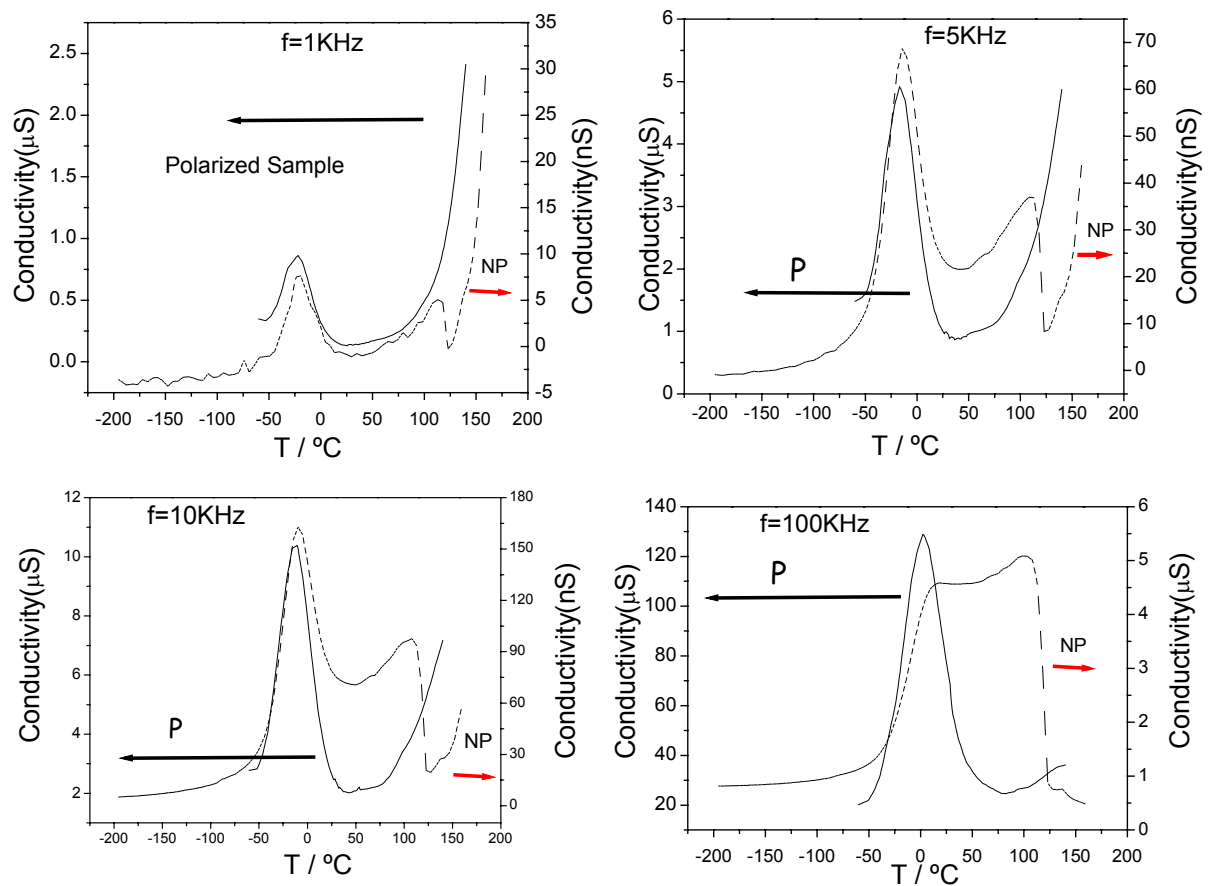


Fig. 3. Conductivity as a function of temperature and frequency (in each figure) for poled (P, left in each picture) and non-poled (NP, right) β -PVDF films. Note the difference in the scale between the values for the poled and non-poled samples

As stated before, the changes in ϵ' in the region of the α_c relaxation seems to be related with strong variations in the dimensions of the samples along a direction perpendicular to the preferred chain orientation above $\approx 70^\circ\text{C}$, due to the release of the orientation induced by the stretching of the film during the processing of β -PVDF (polarized and non-polarized). This shrinking of the sample can neither be related with the onset of mobility within the amorphous nor attributed to the melting of the crystalline structure. In a previous work [16] it was suggested that this effect should be assigned to the onset of 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.

4. IR Spectroscopy

The vibrational spectrum of β -PVDF has been well characterized and several absorption bands characterize the α and β phases of the polymer, the degree of crystallinity and the chain orientation [10,17].

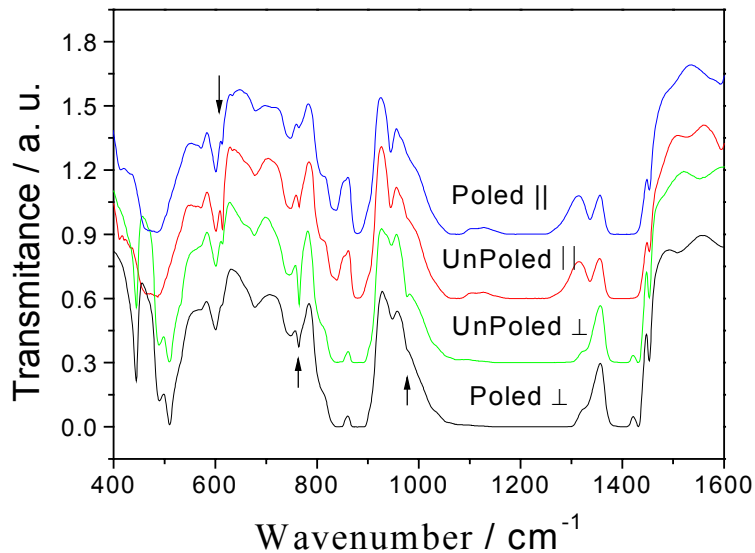


Fig. 4. Detail of the transmittance FTIR spectra at room temperature for poled and non-poled β -PVDF films in parallel and transversal modes. Some of the modes with more relevant changes upon poling are indicated by arrows

The spectra for polarised and non-polarised samples along the stretch direction (\parallel) and perpendicular to it (\perp) are shown in Fig. 4. The general aspect of the spectra is quite similar: neither modes are totally suppressed nor new modes seem to appear due to the poling process. The anisotropic behaviour observed previously for fully polarised samples is also present before the E-field is applied, i.e., the general structure of β -PVDF is determined by the stretching during the processing of the material.

Some particularly relevant modes [10,17] were analysed before and after the poling of the material. The values of the absorbance (A) were determined by the baseline method [18].

The anisotropy of the sample manifests itself in the IR absorption spectrum because the contribution that any particular molecular segment makes to the total absorption of the sample at the frequency of a particular normal mode depends on the angle between the electric field vector of the incident radiation and the oscillating dipole moment vector of that molecular segment. Only the component of the electric field parallel to the dipole moment vector is effective and thus the contribution is greatest when the electric field and the dipole moment are parallel and zero when they are perpendicular to each other.

Producing a preferred alignment of the molecular axes by stretching the sample also produces a certain degree of preferred alignment of the dipole moments. The absorbance of the sample for radiation polarized parallel to the stretching direction, A_{\parallel} , will in general now be different from that for radiation polarized perpendicular to the stretching direction, A_{\perp} , for any absorption peak. The quantity $D = A_{\parallel}/A_{\perp}$ is called the dichroic ratio of the sample for the corresponding mode. The values $D > 1$ indicate that the dipole is termed parallel to the direction of interest, whereas for $D < 1$ the dipole is perpendicular.

The main effect of the poling process is the reorientation of the dipoles along the field direction (direction 3) and transformation of α into β phase, as indicated by the behaviour of the corresponding modes:

- the modes related with the α phase diminish the absorbance both in parallel and perpendicular polarization (e.g., 490, 615 and 763 cm^{-1}),
- the absorbance of modes related to the β phase remains almost unchanged or slightly increases (600, 745 and 840 cm^{-1}),
- the mode at 677 cm^{-1} related to head-to-head and tail-to-tail configurational defects remains unchanged,
- the behaviour of the dichroic ratio for some specific modes identified with bonds well defined with respect to the main chain direction (e.g., $D = 0.28$ and 0.19 for unpoled and poled CH_2 asymmetric and $D = 0.26$ and 0.067 for unpoled and poled CH_2 symmetric stretching).

Further, the fraction of the β phase for each sample can be calculated [19,20]. Assuming that the IR absorption follows the Lambert-Beer law, the A_α and A_β absorbances at 766 and 840 cm^{-1} , respectively, are given by:

$$A_\alpha = \log \frac{I_\alpha^0}{I_\alpha} = K_\alpha C X_\alpha L \quad (4)$$

$$A_\beta = \log \frac{I_\beta^0}{I_\beta} = K_\beta C X_\beta L \quad (5)$$

for a sample with thickness L and an average total monomer concentration C (0.0305 mol/cm^3). The α and β subscripts refer to the α and β phases, I^0 and I are the incident and transmitted intensity radiation, respectively, X is the degree of crystallinity of each phase, and K is the absorption coefficient at the respective wave number ($K_\alpha = 6.1 \cdot 10^4$ and $K_\beta = 7.7 \cdot 10^4$ cm^2/mol).

For a system containing α and β phases, the relative fraction of the β phase $F(\beta)$, can be calculated using Eq. (6):

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta / K_\alpha) A_\alpha + A_\beta} = \frac{A_\beta}{1.26 A_\alpha + A_\beta} \quad (6)$$

The value of this parameter for the poled sample is 0.956 and for the unpoled sample 0.841; this demonstrates the larger amount of β phase in the poled sample for the same degree of crystallinity.

Further, for all samples the relations below were obtained:

$$\Delta_\beta = \frac{A_\beta}{K_\beta L} \quad (7)$$

$$\Delta_\alpha = \frac{A_\alpha}{K_\alpha L} \quad (8)$$

These parameters are related, respectively, to the α and β phases content present in each sample [20]. The values obtained for Δ_β and Δ_α are 32.4 and 1.47 for the poled sample and 12.1 and 2.28 for the unpoled one, respectively. This indicates again an increase of the relative amount of the β phase with poling. This slight increase of the amount of the β phase with poling, together with the preferred alignment of the already existing β phase due to the stretching process with the applied electric field, can also account for the difference in the value of the dielectric permittivity between poled and non-poled samples.

It is worthy to note here that the melting peak of the poled material studied by DSC shows a high-temperature shoulder at c. 167°C, which is close to the maximum peak temperature of the non-poled film. This is probably an indication that the poling process is not fully achieved, and a fraction of the film subsists with the conformation of the non-poled material [16].

The high-temperature behaviour of β -PVDF was previously studied by FTIR spectroscopy [10]. As a general result, whereas the absorbance of some relevant modes in parallel polarization follows a pattern similar to the one observed for the dielectric constant, i.e., the absorbance has a maximum at $T \approx 90^\circ\text{C}$ where ϵ' shows a maximum, the modes observed in the perpendicular polarization show a continuous decrease in the absorbance [10]. A strong reduction of the absorbance in both polarizations above 91°C indicates important conformational changes in the polymeric chains accompanying the shrinkage of the sample. As stated before, the α_c relaxation seems to be in the origin of this shrinkage.

5. Concluding remarks

Dielectric and FTIR experiments have been used in order to characterise β -PVDF films, subjected or not to a previous poling process that improves the piezoelectric characteristics of the material. From the results obtained in this study we can draw the following conclusions:

- The poling process induces a slight increase of the dielectric constant of the material. This increase is attributed both to the preferred alignment of the dipoles of the β phase material and to the α to β transformation due to the application of the electric field.
- The effect of poling on the relaxation mechanism of the polymer is not significant, i.e., poling does not significantly influence the amorphous part of the semicrystalline material.
- Although the general kinetics of the segmental mobility process is not affected (here quantified by the fragility) the non-poled material shows a higher T_g , which points out at more restrictions to the cooperative mobility in the amorphous phase for this film.
- Poling induces a general increase of the conductivity of the material, i.e., charge injection must exist during the poling of the material. On the other hand the mechanism responsible for the ionic conductivity does not seem to be affected by poling.
- From the FTIR spectra, partial rotation of the molecular chains (alignment of the dipoles with the applied field) and conversion of α into β phase are the main effects of the poling field.
- The α to β transformation that occurs by mechanical stretching of the polymer is optimized by the poling field.

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