

ATOMISTIC MODELLING OF PROCESSES INVOLVED IN POLING OF PVDF

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Abstract

Poling processes play an important role in the design and preparation of many ferroelectric materials for practical uses in the field of sensors and actuators. Particularly, the processing of piezoelectric β -poly(vinylidene fluoride) (β -PVDF) involves mechanical stretching in order to transform the extruded α -phase into the β -phase and poling of this later material in order to optimise the piezoelectric response. This poling process affects the orientation of the dipolar moments of the β -chains and improves the α to β transformation.

Poling processes in general and in PVDF in particular are still quite empirical because a firm understanding of the physical processes involved in poling has not been fully established.

In the present work we use a self-consistent quantum molecular dynamics method to study the effect of the electric field on both α and β chains of PVDF. The orientation of the dipolar moments in each chain as a function of an electric field and the accompanying structural modifications due to these reorientations will be the main parameters discussed.

The theoretical results will be used to better understand the changes at a molecular level due to the poling process, as observed in FTIR experiments, performed in poled and non-poled β -PVDF from the same batch.

Keywords: PVDF, poling, infrared spectroscopy, atomistic model.

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1. Introduction

The evolution of modern technologies is fully attached to the evolution of new functional materials. Particularly, the advances in the synthesis and preparation of new polymeric materials with tailored properties have allowed the fabrication of new functional materials having various structures and properties compatible with fabrication of reduced-size lightweight and flexible electronic devices [1].

The most relevant properties of ferroelectric polymers for practical purposes are piezoelectricity and pyroelectricity. Although the piezoelectric and pyroelectric coefficients of ferroelectric ceramics and single crystals are in general larger than those of ferroelectric polymers, the latter are preferred for some applications due to their low cost, low heat conductivity and compatibility with semiconductors.

Poly(vinylidene fluoride) (PVDF) is the prototypical ferroelectric polymer. A wide range of studies have been reported on PVDF and its copolymers, due to its attractive ferroelectric properties [2, 3]. PVDF is a linear fluorinated hydrocarbon with a repeat unit ($\text{CH}_2\text{-CF}_2$), which is semi-crystalline and exhibits different crystalline phases. The β -form provides the best ferroelectric and piezoelectric properties, but the α -form is the more stable one. The α -form is formed during simple crystallization upon cooling from the melt in quiescent conditions [3].

In order to prepare β -PVDF it is first necessary to prepare the electrically inactive material called α_c -PVDF by a stretching process (α to β transformation) – typical stretch ratio 4:1, the sample is stretched up to 4 times its original length – and then subject the sample to large and enduring electric fields (for typical poling conditions the electric field is approximately 6×10^7 V/m). The stretching process alone does not allow a complete α to β transformation even at the highest stretch ratio (7:1). The second step, the so called poling process, consists in the realignment of the dipolar moments by using static electric fields. Before poling, the PVDF sample shows a

random distribution of directions of the dipolar moments. After the poling process has taken place, the dipolar moments show a preferential distribution toward the direction of the applied electric field.

Thus, the β -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 in which the dipoles of all chains are aligned; the maximum polarization obtained for this structure is $P \sim 0.13 \text{ C/m}^2$. Poling and switching are accomplished by applying a large electric field perpendicular to the chains to reverse the direction of the polarization [3].

There are two main models dealing with the dipolar reorientation of the crystallites of the semi-crystalline polymer by considering chain rotations occurring during the poling process: one of the models involves rotation by 180° of each chain around its axis when the electric field is applied; the other model involves also 60° rotations [4]. Whereas the first model predicts extremely large poling times, the latter one is quite fast. Thus, these idealised models may not provide an appropriated explanation of the actual changes observed due to the poling process.

Further, the coupling of the CF_2 dipoles with the electric field, i.e. the rotation of dipoles in the direction of the electric field, is also expected to produce structural changes of different levels. For example, the sequence length of specific conformations, packing of segments in the crystalline unit cell, degree of crystallinity, individual dipole orientation and the overall segmental orientation are all influenced by the electric field. All of these structural changes directly influence the overall electrical properties of the PVDF polymers. An understanding of the field-induced structural changes at molecular level is of importance in order to establish the molecular mechanism associated with the macroscopic electrical properties.

The main objective of the present work is to use a self-consistent quantum molecular dynamics method to study the effect of the electric field at a chain level both in α and β chains of PVDF in order to discuss the molecular level structural changes occurring during the preparation of poled β -PVDF for practical applications.

2. Dynamic simulation method

Because of the nature of the atomic processes involved in mechanical stretching and poling of PVDF, studies of both electronic and atomic motion are essential. In the present work we seek to apply simultaneous geometry optimization and self-consistent electronic structure calculations to α and β PVDF chains with 20 monomer units using the CHEMOS code [5, 6], since for both polymorphs the dipole moment per monomer unit converges to a nearly constant value for chain lengths greater than 17 monomer units. The strategy implemented in this code consists of molecular orbital calculations performed at CNDO (Complete Neglect of Differential Overlap) level to obtain the self-consistent forces on each atom which are used, in parallel, by a molecular dynamical method to perform the atomic motion. The molecular dynamics time step used in the simulation is approximately 1 fs. To be able to simulate mechanical stretching and poling at molecular scale, we have also included the application of external applied electric fields to the PVDF chain and external forces to some of its atoms during the combined self-consistent calculations of both electronic structure and molecular geometry.

The approximate molecular orbital methods, such as CNDO, can be viewed as semi-empiricized versions of density functional theory. If the parameterization is performed by comparison with experimental data rather than with results from a full self-consistent field molecular orbital calculation, one can to some extent take account of the correlation energy. In the calculations

reported here, we have used a set of CNDO parameters to give the best overall fit to the minimal basis set *ab initio* Hartree-Fock calculations.

3. Experimental details

The starting material was a 28 μm 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 material were provided for this work. Therefore the only difference between the two films studied is the poling procedure applied on one of them.

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). The values of the absorbance (A) were measured by the baseline method [7].

4. Results and Discussion

4.1. Theoretical results

The effects of the electric field

Linear chains of PVDF, although electrically neutral, possess a permanent electric dipole moment. As a result, the chains tend to orient their dipole moment with the applied electric field and molecular rotations and distortions are foreseen.

The calculations reported here represent the first attempt to model quantitatively and self-consistently the effects of uniform electric fields on both α - and β -PVDF straight chains and assess the implications of the predictions for the poling process.

We began by studying the electric field effects on α - and β -PVDF chains without any constraints for the assessment of the electrostatic interactions. The constraint in atomic motion due to the presence of neighbouring chains on the crystalline domains of PVDF was considered subsequently by studying the same effect on PVDF chains in which the carbon atoms of both chain ends were prevented from moving out of the molecular axis direction.

For free α - and β -chains and applied electric fields of the order of 5 MV/cm, the main effects predicted were both a rotation of the chain, trying to line up its dipole moment with the direction of the applied field, and a small molecular bending when the angle between the applied field and the dipole moment is smaller or equal to 90 degrees, otherwise a great distortion of the PVDF chain is predicted (see figure 1). Both rotation and distortion of PVDF chains are mainly due to their interaction with the applied electric field. Similar effects have been predicted for PVDF chains with constrained motion of carbon atoms of both chain ends (figures not shown).

Mechanical stretching and poling

In dealing with polymorphic transformations from the α to the β phase, we need to consider two contributions for the induced structural modifications. The first concerns the effects of a mechanical stretching on the α -PVDF chain. The second is due to poling of the stretched chain. Our calculations offer a basis for assessing the relative importance of both contributions for α to β transformation.

The structural modifications of the α -PVDF chain during mechanical stretching can be monitored by applying a force of 8.24 nN to the carbon atoms of both chain ends in opposite directions. These forces stretch the α -chain to the structural modifications displayed in figure 2. As can be seen the transformation from the α -form to the β zig-zag form occurs when the chain length increases by 37%. However, the dipole moment of the stretched chain is much lower than the dipole moment of a β -PVDF chain of the same length.

When an electric field of 50 MV/cm, or greater strength, is applied to the stretched chain perpendicular to the chain axis, a rotation of $-\text{CF}_2$ and $-\text{CH}_2$ around the chain axis in opposite directions was predicted (figure 3). As a result, the dipole moment of the stretched chain increases. The use of larger electric fields than those usually applied in poling experiments was found necessary in order to show the predicted effects with clarity on the time-scale of the simulations.

We have also investigated the effect of high applied electric fields (100 MV/cm) on α -PVDF chains. Our results suggest that such high electric field can cause direct transformation from the α to the β conformation.

4.2 Experimental results: infrared spectroscopy

The piezo and pyroelectricity of PVDF are highly related to the chain orientation and the degree of CF_2 dipole orientation towards the electric field. One of the most suitable experimental techniques to investigate molecular conformation and orientation is infrared spectroscopy [7]. The anisotropy of the sample manifests itself in the infrared 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.

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 (A) 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 vibrational spectrum of β -PVDF has been thoroughly investigated and several absorption bands characteristic of the different bonds, the α - and β -phases and the head-to-head and tail-to-tail defects of the polymer have been identified [8-11]. In particular, vibrational bands at 530 cm^{-1} (CF_2 bending), 615 and 766 cm^{-1} (CF_2 bending and skeletal bending) and 795 cm^{-1} (CH_2 rocking) are identified with the α -phase. Vibrational bands at 510 cm^{-1} (CF_2 bending) and 840 cm^{-1} (CH_2 rocking) correspond to the β -phase.

The dependence of these bands with the degree of crystallinity and/or external fields such as strain [8-10] or temperature [11] allows to monitor possible variations of the chain conformations, orientations and the amount of α and β phases of the material under the effect of these external fields.

The FTIR spectra for polarised and non-polarised β -PVDF samples along the stretch direction (parallel) and perpendicular to it (perpendicular) show the same general features: neither modes are totally suppressed nor do new modes seem to appear due to the poling process (figure 4). On the other hand, the same anisotropic behaviour previously observed for fully polarised samples is also present before the electric field is applied, i.e. the mechanical stretching applied to α -PVDF for the preparation of the electro-active β -PVDF is the main contribution for the α to β transformation and it is also responsible for the preferred chain orientation along the stretch direction.

Comparing the identified modes before and after poling (figure 4) allows us to suggest that the poling has two main effects at a structural level: the reorientation of the dipoles along the field direction and the transformation from the α to the β phase. These poling effects suggested by the experiments were predicted by our theoretical calculations described in section 4.1.

The reorientation effect is also corroborated by the behaviour of the dichroic ratio for some specific modes identified with bonds well defined with respect to the main chain direction. For example, the dichroic ratio for non-poled and poled CH_2 asymmetric stretching is $D=0.28$ and

0.19, respectively, and for un-poled and poled CH₂ symmetric stretching $D=0.26$ and 0.067 , respectively.

The transformation from the α to the β phase predicted by our theoretical calculations is experimentally evidenced by the decrease of the absorbance of the modes clearly related with the α_c -phase (e.g. 490, 615 and 766 cm⁻¹). This decrease is observed both in parallel and in perpendicular modes, ruling out a reorientation of the corresponding modes. Furthermore, the absorbance of the modes identified with the β -phase (600, 745 and 840 cm⁻¹) remains almost unchanged or slightly increases.

The fraction of the β phase present in each of the samples can be also calculated [12, 13]. Assuming that the IR absorption follows the Lambert-Beer law for a film sample, the relation

$$A = \log \frac{I^0}{I} = K C X L \quad (1)$$

is valid for each phase. In this equation, I and I^0 are the incident and transmitted radiation intensities and A_α and A_β the absorbances at 766 and 840 cm⁻¹, respectively, for a sample with thickness L and average total monomer concentration C (0.0305 mol/cm³). The α and β subscripts refer to the α and β phases, X is the degree of crystallinity of each phase and K is the absorption coefficient at the respective wave number ($K_\alpha = 6.1 \times 10^4$ and $K_\beta = 7.7 \times 10^4$ cm²/mol).

Thus, for a system containing α - and β -phases, the relative fraction of the β -phase, $F(\beta)$, can be calculated using the following equation:

$$F(\beta) = \frac{X_\beta}{X_\alpha + X_\beta} = \frac{A_\beta}{(K_\beta / K_\alpha)A_\alpha + A_\beta} = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (2)$$

The value of this parameter for the poled sample is 0.956 and for the unpoled sample is 0.841. This result is in agreement with the behaviour observed for the specific modes related to α - and β - phases: the poling process improved the α to β transformation.

It is worth noting that the application of the electric field does not seem to have any effect of the amount of head-to-head and tail-to-tail configurational defects, as the mode at 677 cm^{-1} , related to them, remain unchanged after poling. This means that the amount of configurational defects, an important factor determining the electrical response of the material, has to be ascribed to the polymerization process, but not to the poling.

It is also important to note here that the melting peak of the poled material studied by DSC shows a high temperature shoulder at ca. $167\text{ }^{\circ}\text{C}$, which is close to the maximum peak temperature of the non-poled film. This is 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. Further, poling does not influence the degree of crystallinity of the material.

5. Concluding Remarks

The main purpose of this work was to study the effects of the application of an electric field in the main phases of PVDF, as this process (poling) plays a central role in the preparation of this type of materials for applications as sensors and actuators.

A theoretical study at a chain level based on a self-consistent quantum molecular dynamics method was applied both to α - and β - chains of PVDF. The main electric field effect predicted is a chain reorientation, with its dipole moment seeking realignment with the applied electric field, accompanied with some structural arrangements. The theoretical results suggest that the α to β transformation can also be achieved without mechanical stretching, when a sufficiently strong electric field is used. When an α -phase sample is subjected to a stretching and a poling process (the most usual way of achieving poled β -PVDF samples ready for application) the stretching is responsible for the main α to β conversion and the poling is responsible for the reorientation of the dipolar moments along the electric field, together with some minor structural rearrangements.

The theoretical results are in accordance with the main results extracted from the FTIR measurements of poled and non-poled β -PVDF samples from the same batch (previously stretched from the α -phase material): the alignment of the polymeric chains and the main α to β transformation is due to the stretching process; the main effect of the poling process is a partial rotation of the molecular chains and a further conversion of α into the β phase. Therefore, the α -to- β transformation that occurs by mechanical stretching of the polymer is optimized by the poling field.

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Figure Captions

Figure 1 – The effect of an uniform electric field of 5MV/cm on a free β -PVDF chain parallel to the x-axis and with its dipole moment making an angle of 176.4 degrees with the z-axis for the applied field parallel to: a) x-axis; b) y-axis and c) z-axis. The PVDF chains were 20 repeat units long. The x and z axes lie in the plane of paper and the y-axis is perpendicular to this plane and points outwards.

Figure 2 – The distortion of α -PVDF chain with 20 repeat units long under the action of a force $F=8.24\text{nN}$ applied to the carbon atoms of both chain ends along the molecular axis (x-axis) in opposite directions. The molecular geometry calculated by self-consistent quantum molecular dynamic is plotted for different times: a) $t = 0$ fs; b) $t = 200$ fs and c) $t = 400$ fs. The x and z axes lie in the plane of paper and the y-axis is perpendicular to this plane and points outwards.

Figure 3 – The effect of an electric field of 50 MV/cm on the stretched chain shown in Figure 2c when the field is applied parallel to y-axis. The snapshots correspond to different times: a) $t = 0$ fs; b) $t = 5000$ fs and c) $t = 10000$ fs. The x and z axes lie in the plane of paper and the y-axis is perpendicular to this plane and points outwards.

Figure 4 – a) FTIR spectra of poled and non-poled samples of β -PVDF in the C-H mode region. The variations of the relative absorbance of the asymmetric and symmetric C-H stretching modes with poling indicates a chain reorientation induced by poling. b) Detail of the 500 cm^{-1} to 800 cm^{-1} spectral region. The decrease of the absorbance of the 615 cm^{-1} and 763 cm^{-1} modes, both related with the amount of α -phase, indicate that the α to β transformation is optimized by the poling process.

Figure 1

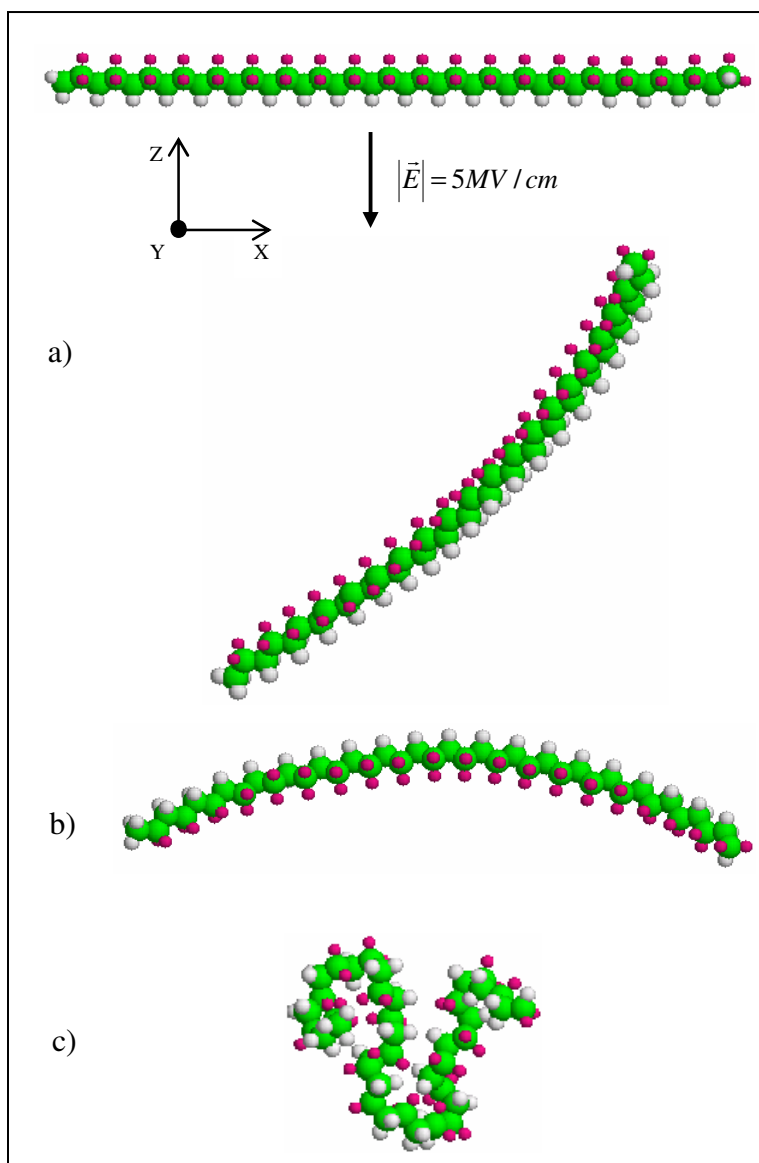


Figure 2

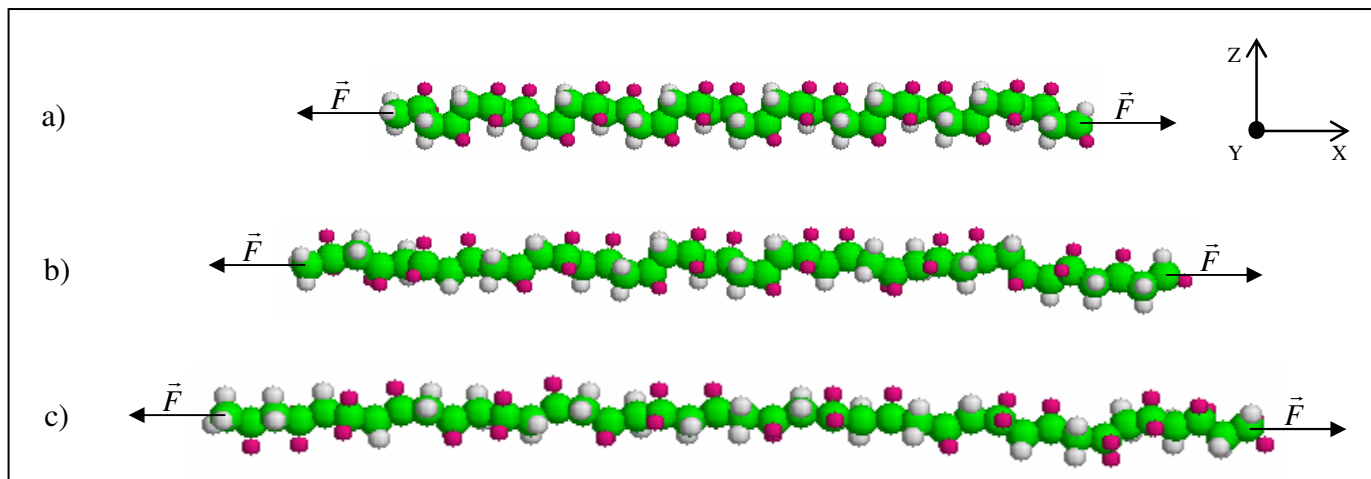


Figure 3

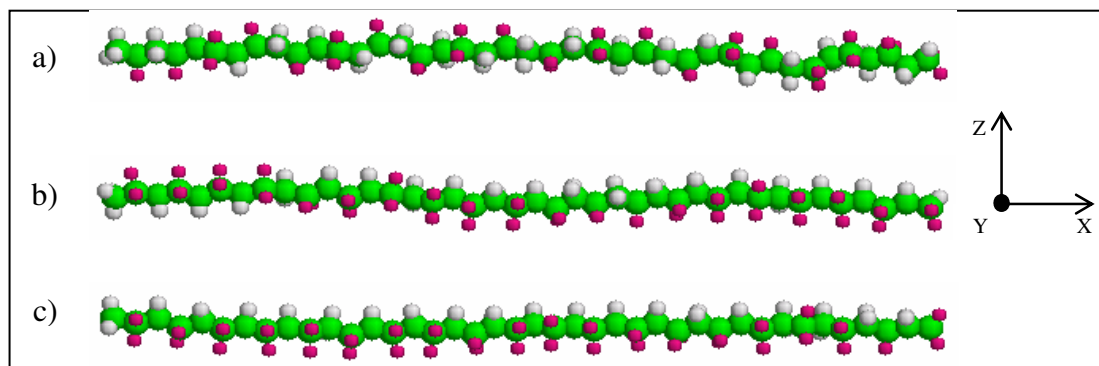


Figure 4

