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2007 J. Phys.: Condens. Matter 19 456210

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First principle calculations of molecular polarization switching in P(VDF–TrFE) ferroelectric thin Langmuir–Blodgett films

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Received 18 June 2007, in final form 7 September 2007

Published 11 October 2007

Online at stacks.iop.org/JPhysCM/19/456210

Abstract

This paper reports first principle calculations and analysis of the molecular mechanism of the polarization switching in polyvinylidene fluoride and its copolymer with trifluoroethylene (P(VDF–TrFE)) using semi-empirical and *ab initio* quantum chemical methods based on the HyperChem 7.5 and Gaussian98 programs. The simulations were performed for different copolymer contents in P(VDF–TrFE)—(70:30), (60:40) and pure PVDF. The calculated values of the dipole moment and average polarization of the molecular chains show a clear hysteresis under varying electric field with polarization saturated at ~ 0.1 – 0.14 C m⁻². The calculated coercive fields (corresponding to the rotation of molecular chains to opposite orientation) are consistent (within an order of magnitude) with experimental data obtained for thin films ($E_c = 5$ – 18 MV cm⁻¹). In the absence of external electric fields, the interactions between several molecular chains lead to the orientation of all dipole moments along one direction parallel to the chain plane. This model corresponds to the PVDF layer on the dielectric surface. For the electric field in the perpendicular direction, all chains are rotated along this direction corresponding to the model of conductive substrate.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In the past, piezoelectric polymer materials based on the poly(vinylidene fluoride–trifluoroethylene) P(VDF–TrFE) copolymer have been widely investigated and used mainly for

transducer and actuator applications [1, 2]. Recently, P(VDF-TrFE) ultrathin films prepared by the Langmuir-Blodgett (LB) technique demonstrated polarization switching on a nanometer scale with the coercive voltage in the order of several volts [3, 4]. Currently, these polymer films are widely explored as promising ferroelectric materials for prospective applications in nanotechnology and microelectronics, e.g. for dense data storage and as non-volatile memory cells [3, 5, 6]. These films demonstrated many advantages such as high polarization values, absence of size effects, and—what is even more important—compatibility with many organic molecules and biomolecules. This can ensure their further use in molecular electronics, nanotechnology and nanomedicine because of the possibility of polarization-driven assembly of biomolecules on their surface [7]. It has been recently shown that small polarization areas (simple dots, lines or more complicated patterns) can be created and imaged by applying small voltages to the conducting tip of the scanning force microscope working in the piezoresponse mode (so-called piezoresponse force microscopy (PFM)) [8]. This opens up many opportunities for using LB films for self-assembly, biorecognition and biofunctional devices, many of them having specific bioferroelectric properties [9]. For example, PVDF membranes are known to have a superior protein binding capacity and they are used widely in automated protein sequencing, amino acid analysis and protein crystal growing [10]. Another opportunity for the application of these films is for adaptive drug administration. Due to the flexibility of PVDF copolymer films combined with possible programmability, they turn out to be a powerful platform for delivering drugs such as potent therapeutic agents whose temporal administrations are vital to their efficacy, and whose effects are naturally amplified by the human body [10].

The switching phenomena in PVDF thin films have been recently studied experimentally using the two-pulse hysteresis technique [11]. The approach, based on the scanning tunneling microscopy (STM) technique [6], has indicated a surface relaxation of the strained copolymer films. Another approach was demonstrated by using the PFM method [7], where the local piezoresponse was tuned by the varying electric field applied to the SFM tip [12, 13]. In both cases, the observed relaxation of polarization after switching was naturally linked to the dipole rotations occurring at the nanoscale. Despite the available experimental data on PVDF films, the mechanism of the molecular reorientation and polarization switching under an external electric field has not been established yet. Moreover, the contribution of ferroelectric molecular chains, layers and domains to polarization switching (especially when the switching occurs in nanovolumes) is not clear at the moment. The understanding of both the molecular mechanism and the origin of ferroelectricity and piezoelectricity in these films is essential in order to design materials with improved properties for different applications. Although there exist several approaches for polarization calculations based on molecular models of PVDF [14–21], no attempts have been undertaken to simulate the rotations of PVDF molecular chains under applied electric fields.

In this paper, we propose a novel approach for molecular switching calculations under electric fields in P(VDF-TrFE) with different TrFE content. To understand the ferroelectric phenomena and to find the molecular mechanism of the polarization switching, the structures of pure PVDF, TrFE and P(VDF-TrFE) were studied. The molecular modeling and quantum chemical calculations were performed and the molecular model structures were built. Additionally, it was necessary to combine computer molecular modeling [20] with local field calculations [22] in order to get the most reliable results. The calculation results were compared with the available experimental data. The performed analysis of molecular formations (chains and layers) is believed to be important for the prediction of the switching behavior of PVDF films and nanostructures based on them.

2. Molecular model approach and computational details

The best known family of ferroelectric polymer films includes PVDF and its copolymer with TrFE. It exhibits several polymorphic crystalline forms: α , β , γ and δ phases, with their formations being dependent on crystallization conditions. The most useful is the polar β phase where PVDF exhibits significant piezo- and pyroelectric properties. This phase can be achieved only in films grown from the solution, by melt crystallization at high pressures or by applying a strong electric field. In its β phase, PVDF has a spontaneous polarization \mathbf{P} of about $0.08\text{--}0.1\text{ C m}^{-2}$ [1, 2]. Similar properties can be obtained in thin polymer films fabricated by the LB technique, but the switching mechanism is quite different [3–6].

The modeling of the molecular structures for PVDF and its copolymer with TrFE was done using computer simulations by the molecular mechanical method (MM+), by the quantum mechanical self-consistent field (SCF) Hartree–Fock (HF) as semi-empirical (PM3), and by *ab initio* (with 6-31G** basis set) methods. For this purpose, the commercial programs Hyperchem 7.5 [23] for MM+ and PM3 methods, and Gaussian98 [24] for *ab initio* HF/6-31G**, were used. The most accurate HF calculations are based on the HF Hamiltonian of the full molecular system with valence double electron wavefunctions including correlation interactions on d-polarization functions for C and F atoms and p-polarization functions for H. For the biggest molecular P(VDF–TrFE) systems we used the semi-empirical SCF methods for quantum chemical calculations (such as PM3 [23]). These methods utilize several experimental parameters to simplify the calculation process. In the case of Gaussian calculations, we created the special file of the investigated molecular model first and then introduced it via direct Linux access to our 32-processor Linux cluster with installed Gaussian98 software.

MM+ is the most general method for molecular mechanics calculations, developed specifically for organic molecules. We use it as a first approximation for the construction of modeling structures. The main approach for both the molecular and quantum mechanics methods used for molecular modeling is to obtain the minimum of the potential energy surface (PES) of a studied molecular system. But in the case of molecular mechanics, calculated force fields use the equations of classical mechanics to describe the PES and physical properties of molecules. Unlike quantum mechanics, molecular mechanics does not treat electrons explicitly. Molecular mechanics calculations cannot describe the bond formation, bond breaking, or role of the electronic subsystems in the determination of the geometry and properties of whole molecules. So, it neglects the system part related to the distribution of the electron subsystem and electron charges, which are described only by quantum wavefunctions. The first principle calculation method expands molecular orbitals of calculated molecular structures into linear combinations of atomic orbitals (LCAOs) for electron wavefunctions and does not introduce any further approximations. HF calculations then approximate the form of a final wavefunction, determining the energy of a modelled system. Using the standard quantum chemical notation for the description and calculation of the electron wavefunction distribution on all atomic orbital and valence bands (so-called split valence basis set in which two basis functions are used for each valence atomic orbital), we must choose the 6-31G** basis set, which includes d orbitals for all heavy atoms and p orbitals for all light atoms (such as H), for our molecular structure. However, this standard calculation with a high level of accuracy usually requires a very long time. Therefore, we tried to compare the calculated data with faster and simpler semi-empirical methods of such first principle calculations using the PM3 approximation. Semi-empirical methods differ mainly in the treatment of electron–electron interactions and using parametrization approaches. For semi-empirical quantum mechanics calculations, we used a simplification that eliminates many of the integrals describing the interactions of electrons. The usual ‘complete neglect of differential overlap’ (CNDO) method neglects the calculation

of all differential overlap integrals [23]. This is the simplest of the SCF methods for semi-empirical quantum mechanics calculations. It is useful for calculating ground-state electronic properties of open- and closed-shell systems, geometry optimization and total energy.

PM3 is based on the so-called ‘neglect of diatomic differential overlap (NDDO)’ [23] approximation with several modifications and on the choice of a wide number of parameters (such as heats of formation or geometries of sample molecules) to reproduce the experimental quantities. PM3 is primarily used for organic molecules, but now it is also used for many groups of elements. It employs empirical parameter sets of atoms suitable for the calculation of polarizability [21, 23], which is readily available for the purpose of present calculations. The optimization of molecular geometry is executed using the Polak–Ribere (conjugate gradient) algorithm, which determines an optimized geometry at the minimum energy point (using PES).

In this paper, we present novel results of the first principle calculations of PVDF polarization under the variation of electric field (hysteresis loops) with different TrFE copolymer contents for the molecular model (consisting of 10 $C_2H_2F_2$ elementary units) using HyperChem 7.5 software. HyperChem calculations on the shorter molecular chains (consisting of one to eight units) were tested using Gaussian98 to compare them with existing experimental and computed data [15–20]. The calculated parameters of polarization hysteresis in P(VDF–TrFE) behavior are also analyzed and compared with available experimental results.

2.1. Numerical modeling of the electrical field effect and hysteresis in P(VDF–TrFE)

In the case of hysteresis loop calculations we used the HyperChem tool for the creation of specific molecular structure in the computational Workspace [23] using necessary options for constructing molecular chains, their orientations, etc. For the modeling of applied electric field HyperChem we used a special option with that allows setting various electric fields and their directions. Using this option we introduced the electric field interaction term into the Hamiltonian of the modeled system and the corresponding equations, which then are solved numerically by HyperChem software. These calculations were done using consequential set-by-step procedure with varying electrical field, and then using single point (SP) calculations (at the fixed position of each atom of the modeled molecules) to determine its initial physical parameters. After that, at each step, full optimization of the structure and energy of the system was carried out using a search for the PES minimum (constructed by HyperChem tool) by the Polak–Ribere (conjugate gradient) algorithm included in another HyperChem option. Finally, we calculated the SP parameters again to determine the final optimized values of the physical properties, such as dipole moment, volume, polarizability etc. This procedure was repeated under every value of electric field applied.

3. Results and discussion

For the investigation of the influence of an external electric field on the dipole moment and polarization of P(VDF–TrFE), we first need to choose and to justify the correct model. Based on the analysis of both our own and literature data, we believe that the PVDF molecular chain $CF_3CH_2-CF_2CH_3$ with 10 structural CH_2CF_2 elemental units is enough for our purpose. Figure 1(a) represents the variation of the dipole moment of VDF monomer chains with increasing number of elemental units. These data are given in table 1 in more detail.

We find that, for the monomer dipoles in finite chains, it quickly converges to their infinite, relaxed chain value (≈ 2 Debye [14–20]). The variation of the calculated polarization values is shown in figure 1(a) on the right vertical axis (more detailed analysis of polarization data in comparison with experimental values was recently published in [20]). Table 2

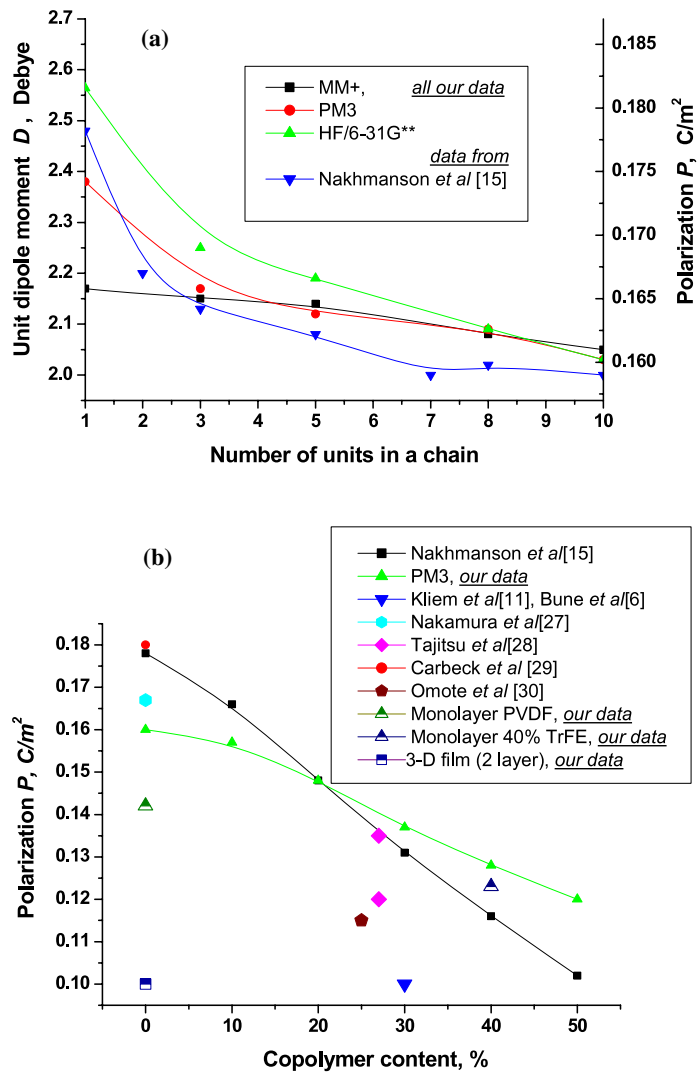


Figure 1. Dipole moment and polarization of the modeled polymer chains: (a) variation of the total dipole moment D (equal to D_3 in the case when the axis OY is oriented along the total dipole moment) in VDF monomer units in finite chains with increasing number of units; on the right axis, variation of the polarization for PVDF with increasing number of chain units (it is calculated for our data using the current volume for each unit from table 1); (b) variation of the polarization P (VDF–TrFE) with increasing TrFE content, including the comparison with other calculated and experimental data.

presents the calculated data of modeled polymer chain with different TrFE content and figure 1(b) demonstrates its variation with TrFE copolymer content in comparison with known experimental data and calculations done by other groups [15]. For our 10 units model we used a $CF_3CH_2-CF_2CH_3$ chain as the PVDF model, and for P(VDF–TrFE) we used a $CF_3CH_2-CFH-CF_2CH_3$ chain as the model, substituting the H atom by an F atom in three sites for 30% TrFE content (conventionally abbreviated as (70:30)) and in four sites for 40% TrFE concentration. Similar substitutions were made for other TrFE contents as well as for the

Table 1. Calculated data for dipole moments, unit volumes and average polarization for *trans* (TTTT) conformation of PVDF chains (optimized data for PM3 and HF *ab initio* methods with relaxed volume).

Structure	Dipole moment (Debye)			Volume (\AA^3)		
	MM+	PM3	HF/6-31G**	Total	Per unit	Polarization (C m^{-2})
Element [$\text{CH}_2\text{-CF}_2$]	2.17	2.38	2.564	47.89	47.89	0.182
Chain (3 elements)	6.46	6.52	6.75	133.83	44.61	0.169
Chain (5 elements)	10.71	10.60	10.95	220.32	44.06	0.166
Chain (8 elements)	16.64	16.80	16.81	346.59	43.32	0.162
Chain (10 elements)	20.52	20.30	20.31	423.82	42.38	0.160
Cell unit (5 chains 3 el.)	32.18	32.16	32.874	649.81	43.32	0.172
Monolayer (6 chains 5 el.)	60.61	58.06	60.569	1443.02	48.10	0.142
Monolayer 2 (2 chains 10 el.)	—	30.88	—	847.52	42.38	0.124
Monolayer 4 (4 chains 10 el.)	—	45.28	—	1694.61	42.37	0.091
3D film (2 layer slab)	57.88	55.12	51.387	1839.09	61.30	0.095
Monolayer with 40% TrFE	79.2	73.46	75.92	2098.79	52.47	0.123

Table 2. Polarization of TTTT-P(VDF-TrFE) chains from 10 elementary units with different contents of TrFE elementary unit component (optimized data only by PM3 methods with relaxed volume).

Content of TrFE (%)	Dipole moment (D)		Volume (\AA^3)		Polarization (C m^{-2})	Polarizability (\AA^3)	Binding energy (kcal mol^{-1})
	Total	Per unit	Total	Per unit			
0	20.30	2.03	423.82	42.38	0.160	37.31	-6304.8
10	20.11	2.01	427.00	42.70	0.157	37.22	-6310.4
20	19.09	1.91	429.80	42.98	0.148	37.13	-6315.9
30	17.72	1.77	432.52	43.25	0.137	37.03	-6321.8
40	16.66	1.67	435.32	43.53	0.128	36.94	-6328.0
50	15.71	1.57	438.13	43.81	0.120	36.85	-6333.1
100	11.148	1.11	452.33	45.23	0.082	36.40	-6359.4
P(TeFE)	0.328	0.03	482.77	48.28	0.002	35.34	-6570.9

entire P(TrFE) and polytetrafluoroethylene P(TeFE) molecular chains. These data were used for making an additional comparison with literature data to justify our models.

All calculated data for the studied molecular nanostructures were obtained from accurate calculations (using several approximations) on the $\text{CF}_3\text{CH}_2\text{CF}_2\text{-CH}_2\text{CF}_2\text{CH}_3$ chain for PVDF structures and on the $\text{CF}_3\text{CH}_2\text{-CF}_2\text{CHF}_2\text{CF}_2\text{CH}_3$ chain for P(VDF-TrFE). The used molecular model corresponds to the β -form of the polymer chain and has a planar-zigzag conformation: all units for PVDF are in the usual *trans*-conformation (TTTT). These chains are aligned in the direction parallel to the b axis of the unit cell, leading to a polar state of the PVDF crystal [1, 20]. For our molecular model the average dipole moment of the chain is oriented perpendicular to the molecular chain axis (its backbone).

The obtained data show that the values of our calculated dipole moments and volume, as well as the polarization for all investigated molecular structures, are consistent with the calculations done by other groups [14–19] and with available experimental data [2–4, 6, 11, 27–30]. The main features of the behavior for all modeled polymer chains have a clear physical meaning. For example, while modeling the polar properties of P(VDF–

Table 3. Calculated values of coercive field for the rotation model of molecular dipole momentum in the opposite direction for different TrFE chain contents in TTTT-P(VDF-TrFE) chains from 10 elementary units.

Composition of P(VDF-TrFE) model (%VDF:%TrFE)	Value of E_c (MV cm ⁻¹)		
	Calculated data		Experimental data
(100:0)	5.3–7.5	0.55	[31] polyvinylidene fluoride (PVDF) thick bulk film
(80:20)	7.7–10.3	1.25	[33] P(VDF:TrFE) (75:25) 60 nm thin spun film
(70:30)	12.5–18.5	7	[11] P(VDF-TrFE) (70:30) 5 nm thin LB films
(60:40)	10.3–12.5	5	[3, 5] P(VDF-TrFE) (70:30) 15 nm thin LB films
(50:50)	4.3–6.4	0.45	[32] P(VDF: TrFE) (65:35) thick spun film

TrFE), we computed copolymer concentration-related changes in the dipole moment of our 10 TTTT monomer unit model. The changes in the TrFE content in the P(VDF-TrFE) chain lead to several effects, owing to the influence of the H atom substitution by fluorine. Clearly, the dipole moment decreases and the volume increases with increasing copolymer concentration. These effects are shown for both the entire chain and for each elementary monomer unit in table 2 and in figure 1. These results are consistent with other studies on P(VDF-TrFE) [16–18] and generally arise from the lattice constant increase and from the evolution of average dihedral angles between monomers. As a result, we have a less compact monomer arrangement in the chain (i.e., the fluorine atoms ‘stick out’ more [14]), but a more stable conformation (shown in the last column of table 2 as a decrease of the calculated energy) at the same conditions (temperature not changed and value of electric field $E = 0$). The effect of extra F atoms in the copolymer favors all TTTT conformations, as also mentioned in [18]. But when the conditions are changed, this leads to the destabilization of conformation and non-equilibrium states of the different parts of the molecular chain. The resulting chain conformation could contain some ‘mixed’ distribution along the chain, containing various additional gauche (G) conformations in combination with TTTT, as shown in [14, 16]. Such an effect is obtained when the modeled system runs in adiabatic conditions [18]. We observe similar effects when the optimization of modeling molecular structures is done under an electric field—transition of the molecular structure under the coercive electric field drives not only whole backbone rotation, but through a series of intermediate states with local distortion of some molecular part. This probably leads to the most complex asymmetrical and non-linear behavior of the calculated values for the coercive electric field with TrFE content variations, which are shown in figures 4–6 and in table 3. This question requires more detailed calculations and analysis. But the main result obtained is that for the (70:30) composition the width of the hysteresis loop is the biggest, meaning that this conformation state is the most stable under electric field variation. These results are very important for practical applications.

We obtain some additional data, e.g. the polarizability of various molecular chains presented in table 2. The comparison with known values shows a good agreement: for example, the value of the polarizability for P(TeFE) is equal to 35.84 \AA^3 [21], while our calculated value is equal to 35.34 \AA^3 .

Figure 2 presents a schematic diagram of the initial molecular model (TTTT chain for PVDF) used in our work for the computer simulations of the electric field influence on the molecular chain state by HyperChem with different approximations for the simulations (‘single point’ (SP) option for a first approximation, and for the most correct one ‘optimized’ calculations, by PM3 and HF). The direction of the applied external electric field E is along the total average dipole moment of the molecular unit and its rotation to the opposite one leads to

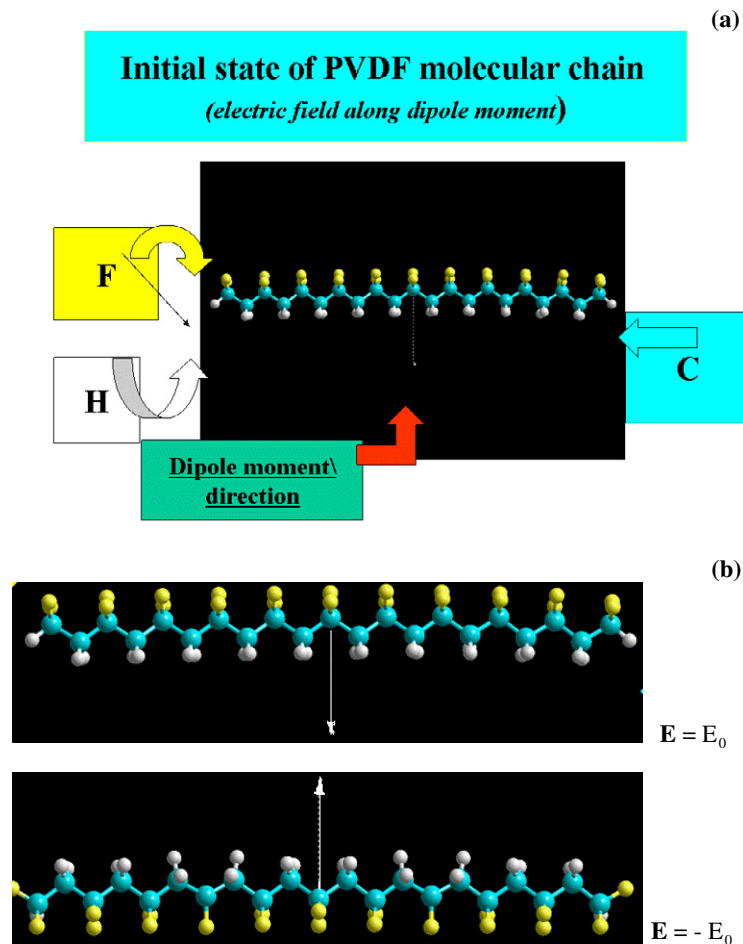


Figure 2. Molecular model of the PVDF chain: (a) explanation of the model; (b) switching of the molecular dipole orientation in PVDF for varying electric fields.

a switching of the molecular dipole. This occurs when the electric field exceeds the critical coercive field E_C . The driving force for the reorientation is the minimization of the total energy of the modeled molecular system, which changes for different dipole configurations. The results of the calculations for the corresponding hysteresis loops are presented in figures 4 and 5.

Figure 3 represents more complicated models of two chains, four chains and two layer slabs used in our simulation. The interaction between PVDF molecular chains (in the absence of an external electric field) leads to the orientation of each molecular dipole moment in the same plane along the cross-section of molecules and corresponding molecular layer. This situation is illustrated in figures 3(a)–(c) for our calculated models with full geometry and energy optimization. The obtained computational data clearly show that PVDF molecular chains prefer to lie with the orientation of their dipole moments along the same plane, crossing all molecules in the case of zero electric field ($E = 0$). Such a situation corresponds to the case of dielectric substrates, when a PVDF molecular chain or layer is attached to the surface without electric charges and external fields. The experimental data for a PVDF chain on a

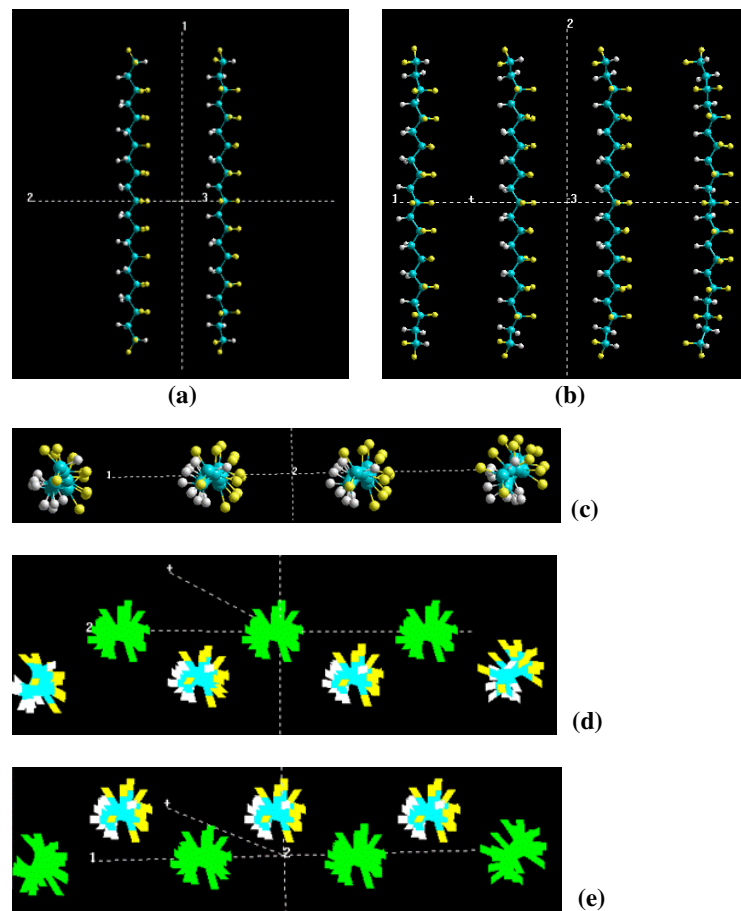


Figure 3. Interaction of the molecular dipoles for PVDF chains: (a) interaction of two chains, (b) interaction of four chains, (c) cross-section of the first molecular layer from four chains, (d) slab of two molecular PVDF layers with frozen upper layer, and (e) same slab as (d) but with frozen down layer.

dielectric KCl surface [25] is qualitatively consistent with our results. This conclusion is in agreement with calculations [17]. In the case of a conductive substrate, even if the external applied electric field is absent, the induced image charges and the corresponding electric field may lead to the orientation of polymer chains in the direction perpendicular to the surface.

Our calculations have shown that the dipole moment of each chain is oriented exactly along the field direction, even if we have several interacting molecular chains in the layer. Such a situation is realized only in the case of the conductive surface (use of a semiconductor or metal electrodes). Without an external electric field, the image charges arising below the substrate surface also influence the PVDF dipole orientation. The preferable orientation of a PVDF dipole is along this field, which is perpendicular to the sample surface in this case. This corresponds to the experimental situation reported for PVDF on graphite [3, 4, 6]. As was emphasized in [4, 25], the PVDF layer adjacent to the conducting electrode could be frozen by induced charges and will not rotate, even if the upper PVDF layers change their orientation under external electric field. This situation may happen in the switching experiments by PFM when the external field is highly inhomogeneous and decays rapidly beneath the surface [7, 26].

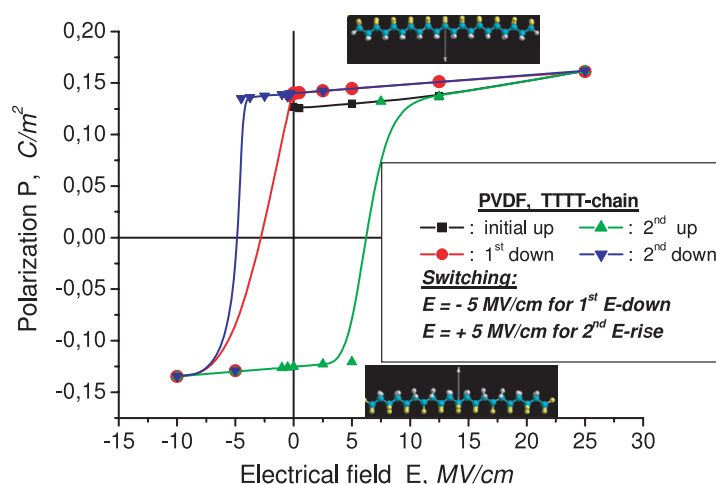


Figure 4. Hysteresis loop of the modeled molecular PVDF chain with 10 monomer units, all in the *trans*-conformation (10-TTTT model, optimized PM3 calculations). The polarization switching corresponds to the change in orientation of the total dipole moment of a chain to the opposite direction under an electric field ($E_c \sim 5 \text{ MV cm}^{-1}$). Insets show the variation of the dipole orientation for the molecular unit.

The modeling of the ‘frozen’ PVDF molecular layer with four chains and the free rotation of other layers was done using HyperChem 7.52 and the corresponding schematic diagram of the PVDF dipole arrangement is presented in figures 3(d) and (e).

Based on this computational analysis, we performed the calculations of the rotation of PVDF and its copolymer in varying electric field that corresponds to the experimental conditions realized in the Sawyer–Tower method or the more complicated two pulse hysteresis loop measurements [6, 11].

The results of the polarization calculations under a varying electric field are presented in figure 4 for the case of the optimized PM3 data. The calculated points have the typical hysteretic shape with the corresponding coercive field (for a pure PVDF chain) of about 5 MV cm^{-1} for this model. Figure 5 shows the calculated data for $P(E)$ for different TrFE contents in P(VDF–TrFE) (molecular chain model). The comparison of single point and optimized calculations shows that for the latter case the coercive field is significantly smaller. It means that the optimized molecular structure has the most stable conformation and a minimum of the energy for an applied electric field compared to the non-optimized ones.

The calculated optimized data for different contents of TrFE are presented in figure 6. It is clear that the hysteresis loop is wider for P(VDF–TrFE) (70:30) as compared to other compositions. It should be noticed that this composition is the most popular one from the point of view of practical applications. Unfortunately, there are no available experimental data for direct comparison. But we can compare our results with some other data presented in table 3.

The comparison of our calculated values with experimental data for P(VDF–TrFE) (70:30) is shown in figure 7(b). Figure 7(a) shows the electronic polarizability on the shape of the hysteresis loop. This corresponds to the notable increase of the polarization under saturation. This value of polarizability is $\sim 37.03 \text{ \AA}^3 - 4.15 \times 10^{-39} \text{ C m}^2 \text{ V}^{-1}$, which agrees with other available data [21]. This result is very important because it shows that the main part of the molecular changes in the electrical field consist of its independent rotation. Figure 7(b) compares the polarization hysteresis without the electronic part with the available experimental

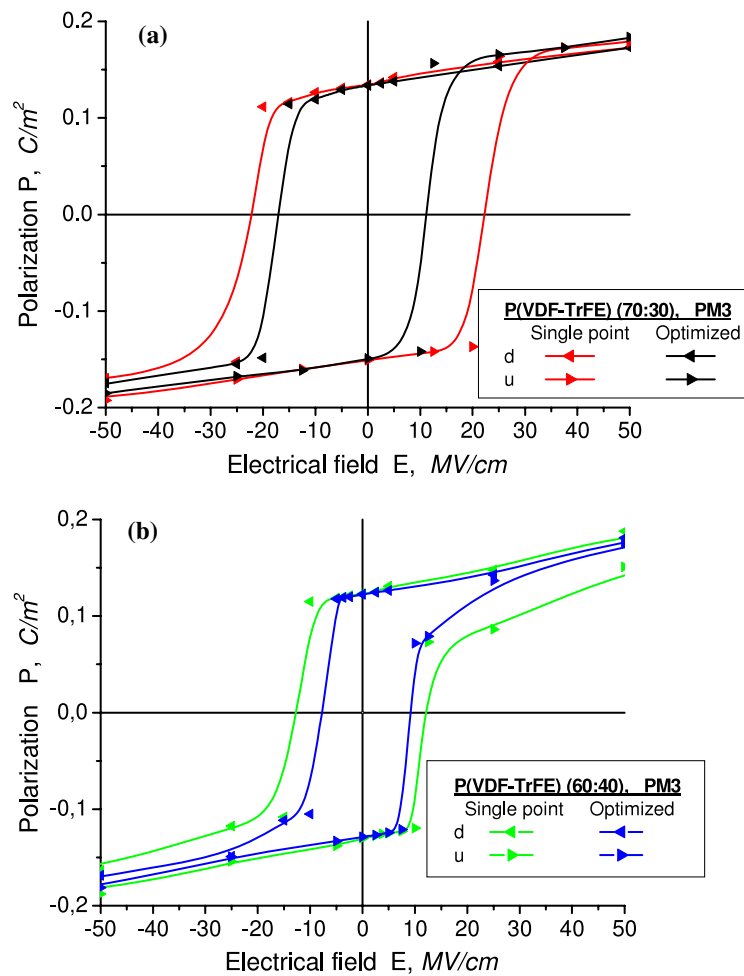


Figure 5. Hysteresis loop of P(VDF–TrFE) in a molecular polymer chain model with different contents of TrFE: (a) 30% of TrFE, (b) 40% of TrFE. Single point (SP) and optimized data of PM3 calculations are presented for comparison.

results. The data agrees with the data [11] on coercive values and common hysteresis loop behavior. Most surprising is the good agreement of the results with the local PFM hysteresis loop measurement [12]. It means that the main part of this switching behavior of the LB film layers under the PFM tip electric field influence is mainly connected with the rotation of the PVDF molecular chains with a comparatively small electronic induced polarization component.

To compare our results with other known data (see table 3), we must point out that the measurements of the coercive field in conventional bulk ferroelectrics have values much smaller than those obtained in our calculation, as summarized in table 3. However, the experimentally measured value of the coercive field (the magnitude of an external electric field required to reverse the macroscopic polarization) is invariably smaller than the *intrinsic* value predicted by the Landau–Ginzburg (LG) mean-field theory [5]. The low *extrinsic* coercive fields observed in bulk ferroelectrics are caused by a localized nucleation of domains with reversed polarization, which then grow and coalesce by domain wall motion. A possible way

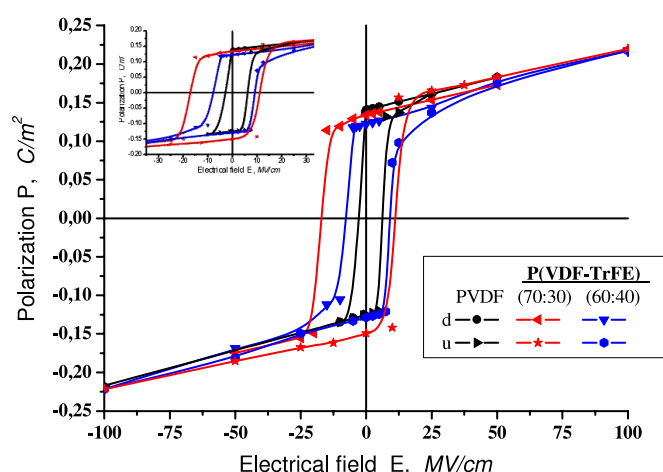


Figure 6. Calculated data of hysteresis loop for different TrFE contents in the molecular polymer chain: wide region of calculated hysteresis loop. The inset shows the central region of the hysteresis loop only. Coercive fields are $\sim 5 \text{ MV cm}^{-1}$ for pure PVDF, $\sim 8 \text{ MV cm}^{-1}$ for 40% and more than $\sim 10 \text{ MV cm}^{-1}$ for 30% of TrFE in P(VDF-TrFE).

to increase the coercive field is to make a particle small enough, or a film thin enough to inhibit nucleation [5]. Such films based on the PVDF ferroelectric polymer and its copolymers showed considerably higher coercive fields, typically 0.50 MV cm^{-1} in bulk and solvent-spinning films (having the thickness $\sim 100\text{--}1000 \text{ nm}$) [31–33]. Nevertheless, only the successful fabrication by Langmuir–Blodgett (LB) deposition of ultrathin films of PVDF and copolymers with TrFE [3–6, 11] showed that the nucleation is inhibited by finite-size effects.

As shown in table 3, films of thickness 15 nm (30 monolayers) or less had the coercive fields of about 5 MV cm^{-1} at $25 \text{ }^\circ\text{C}$, comparable to our calculated data, and are consistent with the theoretical intrinsic value estimations [5]. As shown in [4], nucleation is inhibited in these LB films when the size is below 15 nm, and polarization reversal depends only on the intrinsic ferroelectric properties. Though the nucleation and domain formation do not limit the value of the coercive field, they should play a key role in the switching dynamics.

In our molecular model we have the case of such an ideal system, which is the most suitable to describe switching in highly ordered polymer film, but only without the effect of conducting electrodes and substrate interface.

The calculated values of dipole moment and polarization for P(VDF-TrFE) (60:40) are somewhat smaller than those for P(VDF-TrFE) (70:30) (see figures 1(b) and 6), while the width of the calculated loop is significantly greater. The first result is in agreement with the experimental data [15, 20], and corresponds to the lowering of the total dipole moment of a molecular chain with the substitution of hydrogen by fluorine atoms. In our model, we substituted three of the 10 elementary CH_2CF_2 units (changing to CHCF_3) for the case of (70:30) composition and four of the 10 for the case of (60:40) content. In real experiments, we have many of these molecular chains and each chain consists of random sequences of VDF and TrFE monomer units [18]. Here we use the system of a single molecular chain to simplify our model and to clarify the general effect of an electric field influence on the molecular rotation and switching phenomena. But it must be mentioned that, even for the single molecular chain, the most stable conformation of the model molecule at each step of the simulation is affected by changes of this chain-packing mode of changed units along the chain. So, it means that even

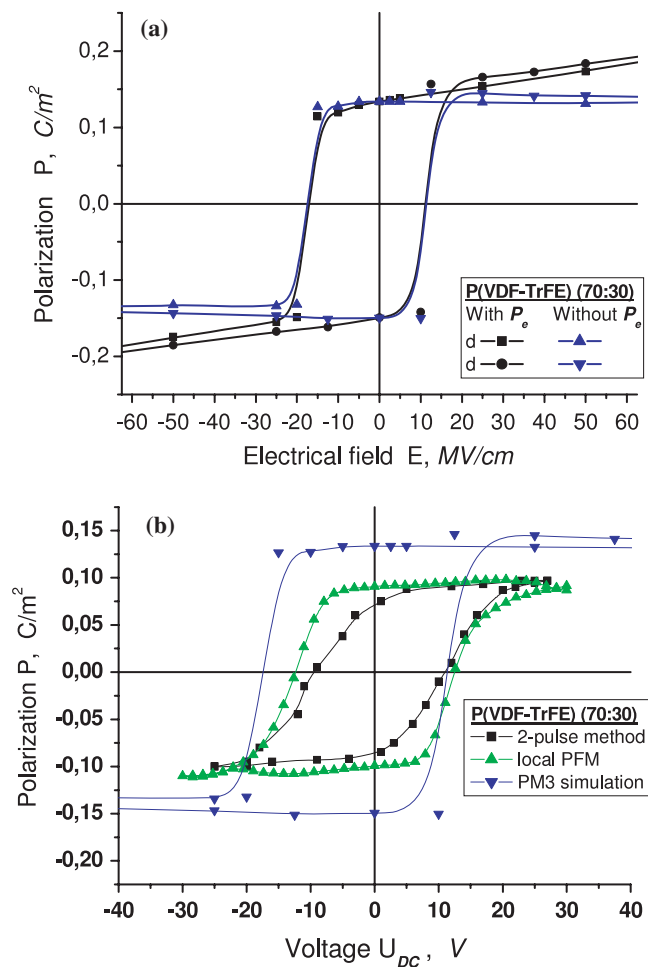


Figure 7. Hysteresis loop of the molecular P(VDF–TrFE) (70:30) model: (a) calculated optimized data with and without contribution of electronic polarizability; (b) comparison of our calculated data with experimental data for the two pulse method [11] and for a local piezoresponse by PFM [12, 26]. Presented PFM data are renormalized to compare with data from [11] for the same P(VDF–TrFE) (70:30) LB thin film sample having 100 transferred monolayers (100 ML) and 64 nm thickness.

if the VDF content is the same, the value of the electrical field for rotational switching of each molecular conformation is dependent on the model used in the simulation, and is affected by changes in such a chain-packing mode for the unit sequence.

The used (60:40) model has a more symmetrical molecular conformation as compared to the (70:30) one. As a result, the hysteresis loop has a more symmetrical shape in this case, while the calculated loop for (70:30) is somewhat shifted along the E axis. This is apparently a result of the asymmetry in the used molecular model. In contrast, a wider loop is calculated for (70:30), meaning that this conformation is the most stable against the varying electric field (figures 4–6). The calculated values of the polarization for the (70:30) model (shown in figure 7 in comparison with experimental data) are slightly higher than those observed in the experiment due to the specific features of our model. Nevertheless, the obtained values of polarizations (0.1 – $0.14 C m^{-2}$) and coercive fields (5 – $18 MV cm^{-1}$) are within the range of observed values.

The coercive field necessary for the rotation of a PVDF molecule by the scanning tunneling microscope [6] is $\sim 2 \text{ MV cm}^{-1}$. The results obtained in [11] yield coercive field values in the range $1.5\text{--}7 \text{ MV cm}^{-1}$ (for different LB film thicknesses) which are comparable with [4] and experimentally observed values are consistent with the constructed molecular model and its interaction with the external electric field. The quality of the model can be further improved by using as many chains with different statistically random VDF sequences as necessary for the realization of the appropriate randomness of the molecular chain-packing and is suitable for many molecular layers, cells and crystals.

Therefore, the proposed mechanism of molecular switching (by a simple rotation model) is important for switching phenomena of PVDF ultrathin films prepared by the LB technique. This result is particularly supported by recent experimental data [11] obtained by two pulse method measurements on the 5 nm ultrathin LB film. The calculated data for the (70:30) copolymer model are the closest to these measured values. Some deviation from experimental results could be explained by our idealized model where isolated rotation is used without taking into account the influence of the substrate and electrodes (additional electrostatic distortions, mechanical deformations and image charges). These issues will be addressed in our future publications.

4. Conclusions

In this paper we have studied the molecular configurations in PVDF copolymers and created computational models that can be applied for thin films prepared by the Langmuir–Blodgett method. The polarization switching under an applied electric field using first principle and semi-empirical quantum chemical methods was described. The polarization hysteresis loops for P(VDF–TrFE) were calculated for the different copolymer contents (70:30) and (60:40) and for pure PVDF. The calculated values of the dipole moment and the behavior of the polarization under a varying electric field show a well defined hysteresis in a qualitative agreement with published data. The values of the calculated polarizations are $\sim 0.1\text{--}0.14 \text{ C m}^{-2}$ and the coercive fields are $\sim 5\text{--}18 \text{ MV cm}^{-1}$. The proposed mechanism of molecular switching (by a molecular chain rotation model) can be used for the explanation of the switching phenomena in PVDF thin films prepared by the LB technique. Presented calculations of the polarization switching provide a novel platform for studying ultrathin ferroelectric polymers at the nanoscale.

Acknowledgments

The work was supported by grants INTAS-05-1000008-8091 and RFBR 05-02-16871. VSB is grateful to Fundação para a Ciência e a Tecnologia (FCT, Portugal) for his fellowship SFRH/BPD/22230/2005 and to DAAD (Germany) for grant No 325/2006. Partial support of the FCT project PTDC/CTM/73030/2006 is also acknowledged. The authors are thankful to Professor V M Fridkin for fruitful discussions of ferroelectric critical size and switching phenomena.

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