

Collective polarization effects in β -polyvinylidene fluoride and its copolymers with tri- and tetrafluoroethylene

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The polar properties of the β phase of polyvinylidene fluoride (PVDF) and its copolymers with tri- and tetrafluoroethylene are investigated theoretically at different VDF-to-copolymer ratios. The calculations show that polarization in such polymers is described by cooperative, quantum-mechanical interactions between polymer chains, which cannot be viewed as a superposition of rigid dipoles. For β -PVDF, the monomer dipole moment is increased by 50% (from 2 to 3 D) as the isolated chains are brought together to form a crystal. In PVDF crystals containing copolymers, we observe a weakly parabolic dependence of monomer dipole moments on copolymer concentration.

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I. INTRODUCTION

Ferroelectric materials are critically important for a wide range of current and prospective technological applications. These are not limited to various electromechanical devices, like sensors, actuators, and transducers, but also include non-volatile ferroelectric memories, high- k dielectrics for modern microelectronics, pyroelectric arrays, and acoustic and non-linear optical devices. Unfortunately, however, there exist only very few classes of materials that exhibit ferroelectric behavior. Perovskite-type ABO_3 metal oxides (e.g., $BaTiO_3$ or $KNbO_3$), comprising the most important class of ferroelectric materials, are widely known for their strong polarization and excellent piezoelectric response. Still, their usefulness is limited by heavy weight, brittleness, and substantial costs of device manufacturing. Furthermore, the highest polarization and piezoelectricity are achieved in perovskites containing lead (e.g., $PbZr_{1-x}Ti_xO_3$), while the properties of lead-free compounds, especially when grown as thin films, are more modest.¹ Ferroelectric polymers, on the other hand, exhibit properties almost *complementary* to those of perovskite-type oxides. In addition to being respectable piezo- and pyroelectrics, they are light, flexible and nontoxic,²⁻⁷ which is particularly important in the view of the recent interest in new, more efficient, and environmentally friendly materials.

Polyvinylidene fluoride (PVDF), $[-CH_2-CF_2-]_n$, the most well-known ferroelectric polymer, is a complex material that is usually synthesized as a mixture of ordered and disordered phases, and requires some postprocessing in the form of stretching and poling to become ferroelectric (see, e.g., Figs. 3–5 in Ref. 2 for a good illustration). The most polar all-*trans* β phase of PVDF, shown in Fig. 1, has been extensively studied by theorists during the past three decades, which resulted in a number of empirical models for polarization in β -PVDF.⁸⁻¹⁴ Since, even after the aforementioned postprocessing procedure, β -PVDF is usually only

50% crystalline,¹⁵ until very recently there had been no certainty about the value of polarization in the fully crystalline material. As can be seen from Table I, the various models do not agree with each other, which recently motivated us to apply modern *ab initio* techniques to compute spontaneous polarization in β -PVDF.¹⁶ Our results ($P_3^{sp}=0.178$ C/m²) clearly show that the majority of the previous models, fitted either to experiment or to a simple sum of the bond-dipole moments in an *individual* VDF monomer^{4,7} (≈ 2 D), underestimate the strength of the dipole-dipole interaction in this material. The polarization obtained in Ref. 13, utilizing a force field developed by fitting to Hartree-Fock calculations for finite PVDF chains,¹⁷ is the only notable exception,

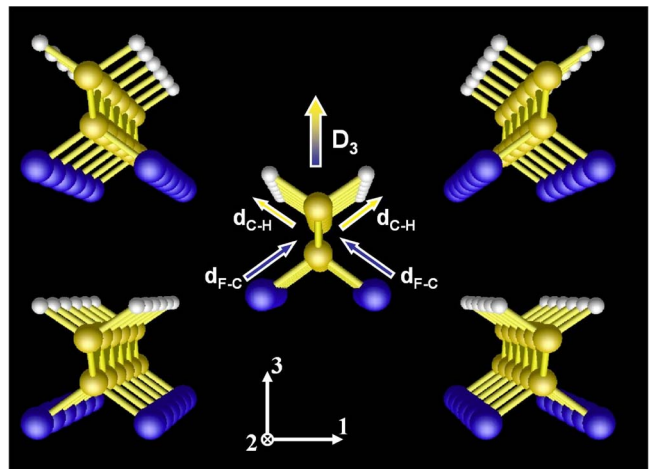


FIG. 1. (Color online) The structure of the crystalline β phase of PVDF. The polar-covalent nature of the F—C and C—H bonds leads to polarization in the VDF monomer, directed perpendicular to the carbon backbone; d_{F-C} and d_{C-H} are the bond-dipole moments. The unit cell coordinate system is shown at the bottom with “2” and “3” being the backbone and polarization directions, respectively.

TABLE I. Polarization P^{sp} in β -PVDF computed with various theoretical models. C is the crystallinity of the material.

Model	Year	C (%)	P_3^{sp} (C/m ²)	Ref.
Rigid dipoles		100	0.131	4
Kakutani, Mopsik and Broadhurst	1970–75	100	0.22	8 and 9
Tashiro <i>et al.</i>	1980	100	0.140	10
Purvis and Taylor	1982–83	100	0.086	11
Al-Jishi and Taylor	1985	100	0.127	12
Carbeck <i>et al.</i>	1995	100	0.182	13 and 14
Nakhmanson <i>et al.</i>	2004	100	0.178	16
Experiment		≈ 50	0.05–0.08	

stressing the idea that “*ab initio* input” is required to produce an accurate model. However, neither of the previous investigations studied the electrostatic interactions among monomers in β -PVDF-type polymer structures at the detailed level required to fully elucidate the intricacies of their polar behavior.

Moreover, although the ideal β -PVDF structure serves well as a simple model for basic understanding of the polar nature of ferroelectric polymer crystals, it is quite different from the polymeric structures used in actual device manufacturing. Since poor crystallinity of “pure” PVDF degrades its polar properties, it is usually mixed with trifluoroethylene (TrFE), [—CHF—CF₂—], and tetrafluoroethylene (TeFE), [—CF₂—CF₂—] (shown in Fig. 2) to produce device-grade materials. Naturally, compared to VDF, TrFE and TeFE monomers exhibit lower or no polarization. However, such P(VDF-copolymer) systems can be grown with 90% or better crystallinity,^{3,18–21} which results in stronger polarization and piezoelectric response than that of 50% crystalline PVDF. In addition, these structures can be grown in the form of ultrathin films²² and have other important electromechanical properties, e.g., giant electrostriction.²³ However, it turns

out that realistic *ab initio* models of polarization in these materials are required to explain the peculiarities of their behavior and to open avenues for development of better polymeric ferroelectrics for modern technological applications.

In order to fully understand the physics of polarization in crystalline β -PVDF and in P(VDF-copolymer) systems one needs to answer the following questions. (a) What are the main “building blocks” governing the polar properties of a polymer-ferroelectric crystal: are these individual monomers, chains, or, possibly, something else? (b) What is the “natural value” of a structural unit dipole moment in a given environment (individual molecule, chain, crystal)? (c) What happens to this value when the environment changes, e.g., when the VDF-to-copolymer concentration changes?

The rest of this paper is organized as follows. Section II briefly reviews the formulation of modern polarization theory in terms of Wannier functions and presents the details of the numerical techniques that were used to compute polarization. In Sec. III we discuss the results of our calculations, progressing from individual monomers to chains and then to P(VDF-copolymer) crystals. Finally, Sec. IV presents the summary and the conclusions.

II. METHODOLOGY

A. Modern theory of polarization

In an infinite periodic solid, the macroscopic polarization can be written as the sum of ionic and electronic terms:

$$\mathbf{P} = \mathbf{P}_{\text{ion}} + \mathbf{P}_{\text{el}} = \frac{e}{V} \sum_{\tau} Z_{\tau} \mathbf{b}_{\tau} - \frac{1}{V} \int_V \mathbf{r} \rho(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where V is the volume of the unit cell, Z_{τ} and \mathbf{b}_{τ} are the charge and position of the τ th atom in the cell, and $\rho(\mathbf{r})$ is the cell-periodic density of electron charge. Since the position operator \mathbf{r} lacks the periodicity of the system and $\rho(\mathbf{r})$ is usually delocalized in covalent or polar-covalent structures, the second term of the equation has to be regularized before further use. The *de facto* standard approach for such a regularization was proposed by the modern theory of polarization, put forward about a decade ago.²⁴ The theory provides two complementary techniques to obtain \mathbf{P}_{el} , depending on the particular representation for $\rho(\mathbf{r})$, which can be expanded

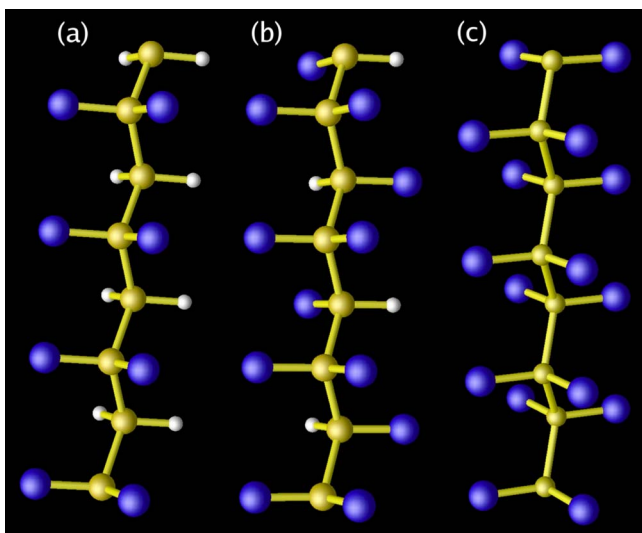


FIG. 2. (Color online) Chain models for PVDF and copolymers. (a) PVDF chain in all-*trans* conformation. (b) Poly-TrFE chain with alternating hydrogens. (c) Poly-TeFE chain.

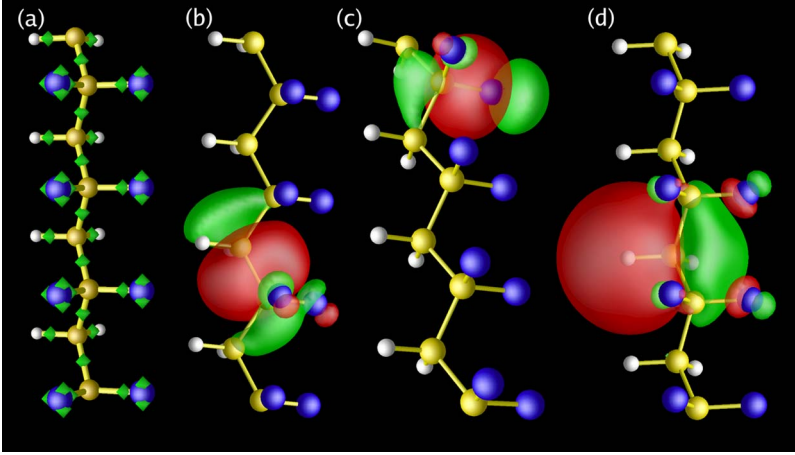


FIG. 3. (Color online) MLWFs and their charge centers computed for an isolated infinite β -PVDF chain. (a) Diamonds mark the positions of the MLWF charge centers on the chain. (b)–(d) Typical MLWFs localized on carbon-carbon, carbon-fluorine, and carbon-hydrogen bonds, respectively.

into either a sum of occupied Bloch states $\psi_{ik}(\mathbf{r})$ or a sum over occupied Wannier functions (WFs) $W_i(\mathbf{r})$ (for paired-electron systems):

$$\rho(\mathbf{r}) = -\frac{2e}{(2\pi)^3} \sum_{i \text{ occ}} \int_{BZ} d\mathbf{k} |\psi_{ik}(\mathbf{r})|^2 = -2e \sum_{i \text{ occ}} |W_i(\mathbf{r})|^2. \quad (2)$$

Utilizing the Bloch-state representation for $\rho(\mathbf{r})$ leads to a widely known “Berry-phase” expression for electronic polarization, which works well when only the *total* value of \mathbf{P}_{el} is needed. If, however, one is interested in *contributions* to polarization originating from various structural units in the system, e.g., individual dipole moments of monomers in a polymer crystal, or “layer-by-layer” polarizations in a perovskite ferroelectric, these values cannot be extracted from a single Berry-phase computation.²⁵

On the other hand, the WF representation for $\rho(\mathbf{r})$ produces an especially transparent formula for \mathbf{P}_{el} useful for polarization analysis in “modular” systems:²⁶

$$\mathbf{P}_{\text{el}} = -\frac{2e}{V} \sum_{i \text{ occ}} \langle W_i | \mathbf{r} | W_i \rangle = -\frac{2e}{V} \sum_{i \text{ occ}} \langle \mathbf{r}_i \rangle, \quad (3)$$

where $\langle \mathbf{r}_i \rangle$ are the centers of charge of WFs $W_i(\mathbf{r})$. Compared to Eq. (1), \mathbf{P}_{el} in the equation above is well defined for sufficiently localized $W_i(\mathbf{r})$. A general algorithm, outlined in Refs. 27 and 28, exploits the nonuniqueness of the unitary transformation connecting Bloch orbitals $\psi_{ik}(\mathbf{r})$ and WFs $W_i(\mathbf{r})$ to iteratively find maximally localized Wannier functions (MLWFs). The sum of quadratic spreads of the Wannier probability distributions $|W_i(\mathbf{r})|^2$,

$$\Omega = \sum_{i \text{ occ}} [\langle r_i^2 \rangle - \langle \mathbf{r}_i \rangle^2], \quad (4)$$

is used as a minimization criterion. In general, this transformation has a k -space dependence, which makes calculations more complicated. However, for the studies of polymer chains and crystals we can use large supercells, in which the Γ -point approximation for the k -space summation is well justified. In this particular case, computing MLWFs is reduced to finding a single orthonormal transformation matrix, which

can be done very efficiently by a number of numerical techniques.^{29,30}

As already pointed out above, expression (3) is particularly useful for studies of “modular” systems, like polymer chains or crystals. Because in such systems each structural unit (monomer) is connected to only a single neighbor from above and below, one can easily identify the WF centers “belonging” to the unit as well as the ones that are shared with the neighbors. Combining Eqs. (1) and (3), a simple formula for the structural unit’s dipole moment can be obtained:

$$\mathbf{D} = e \sum_{\tau \in \text{unit}} Z_{\tau} \mathbf{b}_{\tau} - 2e \sum_{i \in \text{unit}} \langle \mathbf{r}_i \rangle. \quad (5)$$

Here we implicitly assume that contributions from the shared centers are included with weights of one-half. This expression will be extensively used for the studies of the monomers’ dipole moments, presented in the next section.

B. Computational details

For all the calculations presented here, we used an *ab initio* multigrid-based total-energy method, which employs a real-space grid as a basis³¹ and three-dimensional periodic boundary conditions. The exchange-correlation interaction was described by the generalized gradient approximation of Ref. 32. We employed norm-conserving pseudopotentials^{33,34} generated by the FHI98PP package.³⁵ The Γ -point-specific routine for calculating the MLWFs was developed using the simultaneous diagonalization algorithm of Ref. 30. This algorithm allows for bypassing the computation of the WFs if only their charge centers are needed.

Although van der Waals interactions are neglected in density functional theory (DFT), the cohesion in highly polar structures, such as β -PVDF, is dominated by dipole-dipole interactions, which are well described by DFT.

For cell-volume relaxations we used a plane-wave-based PWSCF code³⁶ and ultrasoft pseudopotentials,³⁷ to simultaneously relax the cells and ionic positions in the P(VDF-copolymer) systems. The optimized cells were then used in WF calculations with the grid-based method.³⁸

An example result of a MLWF calculation for an isolated infinite β -PVDF chain is presented in Fig. 3. The leftmost

TABLE II. Average monomer dipole moments in the infinite PVDF, PTrFE, and PTeFE chains. Values computed at β -PVDF chain-backbone lattice constant (2.56 Å/unit) as well as at the relaxed lattice constant are shown.

	D_3 , $c=2.56$ Å/unit (D)	D_3 , relaxed c (D)	Relaxed c (Å/unit)
VDF	2.00	2.00	2.560
TrFE	0.78	0.75	2.667
TeFE	Nonpolar	Nonpolar	2.749

panel (a) shows MLWF charge centers on a chain, with a single center located on every σ bond in the system and three additional centers localized near each fluorine atom. The remaining three panels show MLWFs localized on different types of σ bonds: (b) carbon-carbon, (c) carbon-fluorine, and (d) carbon-hydrogen.

III. RESULTS AND DISCUSSION

A. From a monomer to a chain

The first question to be addressed is what happens to the value of the monomer's dipole moment D given by Eq. (5), as an increasing number of monomers is being united into a chain.

In order to answer this question, we computed average dipole moments of VDF, TrFE, and TeFE structural units in finite $\text{H}-[\text{CH}_2-\text{CF}_2]_n-\text{H}$, $\text{H}-[\text{CHF}-\text{CF}_2]_n-\text{H}$, and $\text{H}-[\text{CF}_2-\text{CF}_2]_n-\text{H}$ polymer chains for $n=1, \dots, 8$. The chains were relaxed to ionic forces of less than 0.025 eV/Å in large supercells, so that the distance between each chain and its periodic images was approximately 10 Å. In addition, we computed the same dipole moments for the limiting case of infinite chains, like the ones shown in Fig. 2, in supercells containing four or eight structural units. The calculations were performed at both β -PVDF (2.56 Å per structural unit) and the fully relaxed lattice constants c along the chain-backbone direction. The results are presented in Table II. Our value of the VDF dipole moment is in excellent agreement with results in the literature.^{7,39}

Figure 4 shows the average values of VDF, TrFE, and TeFE monomer dipole moments in finite hydrogen-terminated chains. Since the terminating hydrogens alter the values of the dipole moments of the first and the last units in the chain, we included two sets of curves for each monomer type, with the chain-end units included and excluded from the averaging process. In both cases the curves for the monomer dipoles in finite chains quickly converge to their infinite, relaxed c , chain values on the right border of the figure. In general, we observe that apart from very short chains ($n=1-3$), the average value of the monomer dipole moment is very close to its infinite-chain limit. This shows that in a single chain there is no polarization enhancement due to the growing electric field produced by the neighboring units.

Similar results are obtained for polymer chains where one or more monomers are substituted by copolymers. The results of such calculations for the chains where one of the

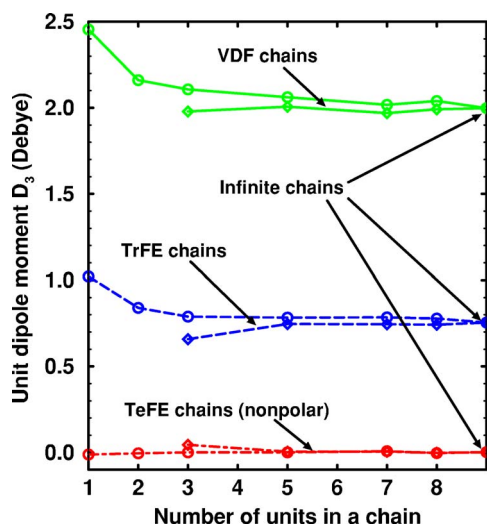


FIG. 4. (Color online) Variation of the dipole moment D_3 in VDF, TrFE, and TeFE monomer units in finite chains with increasing numbers of units. Dipole moments obtained by averaging over all n monomers in a chain are shown as circles, while diamonds represent the average moments when the end units (i.e., those in direct contact with terminating hydrogens) are excluded. The dipole moments of the monomers in infinite chains are shown on the right.

eight units in the supercell was substituted by TrFE, TeFE, or an inverted VDF, also known as the head-to-head, tail-to-tail (HHTT) defect, are presented in Fig. 5. All of these cases demonstrate that introduction of an isolated defect, even as drastic as HHTT, into a β -PVDF chain does not seriously affect the polar states of the other units in the chain, except maybe the nearest neighbors of the substituted unit. On the other hand, a copolymer unit or a HHTT defect substituted into the chain keeps its own characteristic features fairly intact or even amplifies them. For example, a TrFE unit embedded into the chain has the same D_3 component as in a PTrFE chain and it also retains its large D_1 component. Similarly, the HHTT defect has its D_3 component increased to nearly 3 D.

We can conclude that (i) in general, individual monomers in infinite isolated chains prefer to “keep their identities,” and (ii) various kinds of elaborate polarization patterns in a chain can be created by assembling the appropriate monomer types. In this respect a $(-\text{[CH}_2-\text{CF}_2]-\text{[CHF}-\text{CHF}]-)_n$ system will be particularly interesting, with VDF units having large D_3 and $[-\text{CHF}-\text{CHF}-]$ units large D_1 projections. Of course, such level of precise monomer manipulation has not yet been achieved, but it may become possible in the future.

B. From a chain to a crystal

After understanding the behavior of monomer structural units in isolated chains, we investigate the “structural assembly” of chains. Starting from an isolated infinite chain, we gradually bring the chains together until a crystal is formed.

We computed the average VDF dipole moments for a system containing four β -PVDF chain segments of four units each in a pseudohexagonal arrangement in an orthorhombic

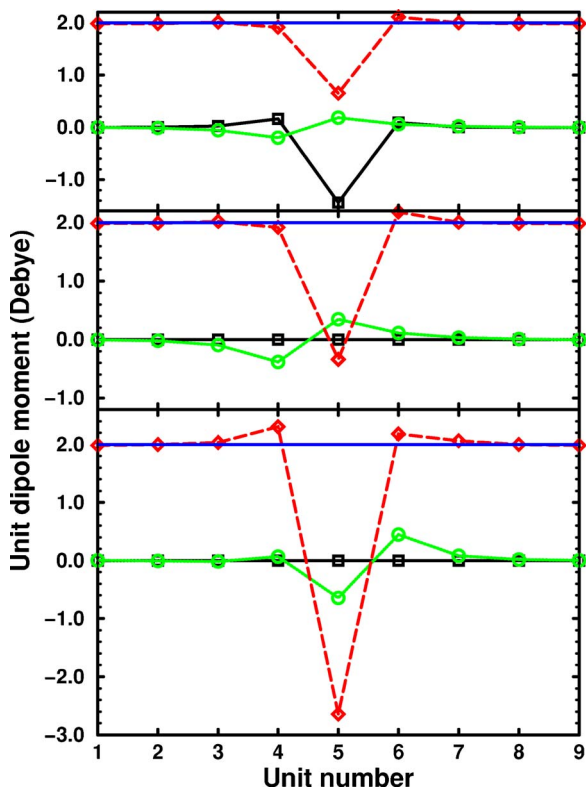


FIG. 5. (Color online) Structural unit dipole moment components D_1 (squares), D_2 (circles), and D_3 (diamonds) in infinite isolated β -PVDF chains where one of the units (number 5 in this figure) was substituted by TrFE (top panel), TeFE (middle panel), and inverted VDF (bottom panel). Horizontal lines at 2 D in each panel mark the D_3 value of the VDF unit in a β -PVDF chain with no substitutions.

supercell. The lattice constant c in the backbone direction was fixed at $2.56 \text{ \AA}/\text{unit}$, while the lattice constants a and b were allowed to vary. Two calculations were carried out for each particular interchain distance (i.e., a combination of a and b). In the unrelaxed case, the ions were held fixed (in the same arrangement as for the relaxed isolated chain), so that only the electronic degrees of freedom were allowed to vary. In the relaxed-chain case, both the electrons and the ions were allowed to relax to their minimum-energy positions. The ionic forces in the relaxed configuration were smaller than 0.025 eV/\AA . The polarization of the crystalline structure was computed at the experimental lattice constants of $a=8.58 \text{ \AA}$, $b=4.91 \text{ \AA}$ (polarization direction), and $c=2.56 \text{ \AA}$ (backbone direction) for the primitive orthorhombic cell with two structural units. The actual supercell used in the calculations for the crystal contained $1 \times 2 \times 4$ primitive cells.

The results of the calculations are presented in Fig. 6, where the average VDF dipole moments are plotted vs the interchain distance. The most striking feature of these curves is a dramatic increase in the VDF dipole moment as the chains are brought out from the noninteracting limit and assembled into the crystalline β -PVDF structure. A similar comparison was also performed in Ref. 13, using the *ab initio*-fitted force field.¹⁷ Although the values of VDF unit

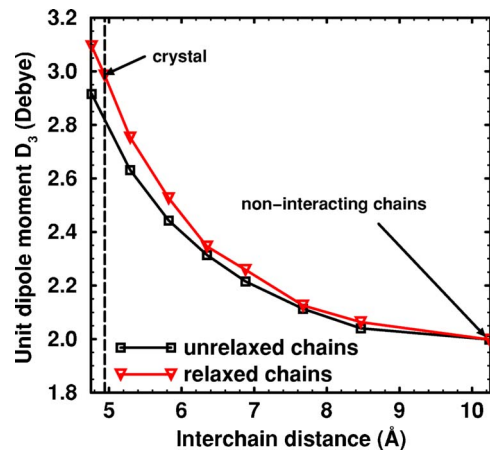


FIG. 6. (Color online) Average D_3 component of the VDF unit dipole moment in an infinite β -PVDF chain as the chains are brought together to form a crystal. See text.

dipole moments in these calculations do not perfectly agree with our results, the degree of the polarization enhancement between the isolated chain and the crystal is nearly the same as the one obtained in this work.

Apart from the fact that the “collective polarization” enhancement in the β -PVDF crystal is much stronger than that in the isolated chain, the polarization curves of Fig. 6 show why many of the other empirical models in Table I give polarization in β -PVDF that is too low. Apparently, using the value of the VDF dipole moment of an isolated chain *in a crystal* (which is tempting since the former is well known) completely neglects the “collective polarization” enhancement effect. *Ab initio* calculations unequivocally show that this effect is very large and has to be accounted for in order to get an accurate value for polarization in a fully crystalline β -PVDF. However, in addition to simply computing the magnitude of the polarization enhancement, our approach allows for an effective decoupling of the electronic and ionic contributions to it. If we compare the curves for the unrelaxed and relaxed chains in Fig. 6, we notice that even in the former case, i.e., with ions pinned in place, we still obtain 80% of the total polarization enhancement effect, indicating that the nature of the polarization increase is mostly electronic. Indeed, the calculations show that ionic relaxations only lead to an approximately 1° narrowing of the F—C—F angle in a VDF monomer, leaving all of the bond lengths practically unchanged. On the other hand, the centers of WFs that are attached to a monomer’s C—F and C—H bonds shift by 1–3 %. The magnitudes of these shifts are on the order of 0.1 bohr, which is very small, but sufficient to produce the observed dipole-moment change of about 1 D.

C. Crystal with copolymer units

Starting from the β -PVDF crystal we substituted some of the VDF units by TrFE and TeFE to create realistic models of P(VDF-copolymer) crystalline systems and to study their structural and polar properties. Since TrFE and TeFE structural units contain more “bulky” fluorine atoms than VDF,

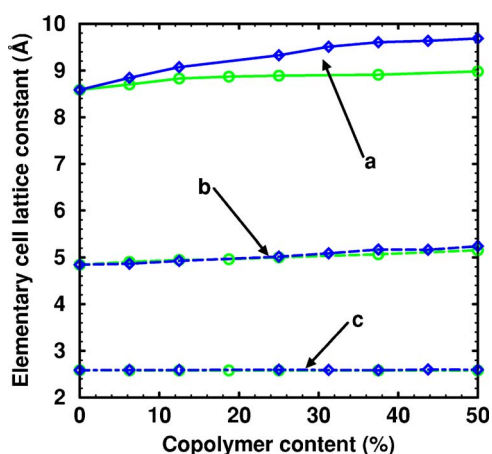


FIG. 7. (Color online) Evolution of an elementary two-unit orthorhombic cell lattice constants with changing copolymer concentration. Circles and diamonds represent the P(VDF-TrFE) and P(VDF-TeFE) families, respectively.

simultaneous relaxations of the cells and ionic positions in the P(VDF-copolymer) systems are required. In these calculations, one to eight units in the initial β -PVDF crystal were changed into TrFE or TeFE, which corresponds to copolymer concentrations of 6.25–50%. Each P(VDF-copolymer) structure was relaxed to stresses of less than 0.5 kbar and ionic forces of less than 0.025 eV/Å.

In Fig. 7 we show the changes in the lattice constants (reduced to the primitive β -PVDF orthorhombic cell with two units) as VDF units in the system are being turned into either TrFE or TeFE. Clearly, there is no expansion along the direction of the carbon backbone—the only “rigid” direction in the system—and only a weak expansion in the polarization direction in both families of models. This leaves the bulk of volume expansion to occur through the increasing lattice constant a . For the 50-50 VDF-to-copolymer concentration, in P(VDF-TrFE) and P(VDF-TeFE) systems a grows by 4.6% and 12.8%, respectively. In Fig. 8 we plot the evolution of an average dihedral angle between the neighboring units in the system with growing copolymer concentration. For β -PVDF our calculations produce dihedral angles that are very close to 180° , which means that neighboring units on a chain are all perfectly aligned in the polar direction and agrees with the previous first-principles calculations of Ref. 17. This result does not support the model of Hasegawa *et al.*,⁴⁰ who suggest that in β -PVDF monomers in a chain are tilted by 7° with respect to each other due to the steric hindrance of the neighboring fluorine atoms. (The tilt angle is defined as 180° minus the dihedral angle.) However, our calculations show that β -PVDF does develop tilts when some units are changed into TrFE or TeFE. In fact, the presence of only a few TrFE monomers (one or two units in the 16 unit cell, equivalent to the defect concentration of 5–10%), which have nonzero dipole moment components along the “3” and “1” directions, produces a tilt of around 7° . On the other hand, dihedral tilts develop more gradually for the TeFE monomers that do not possess nonzero dipole moment components along the “1” direction. At 50–50 VDF-to-copolymer ratio, both P(VDF-TrFE) and P(VDF-TeFE) have

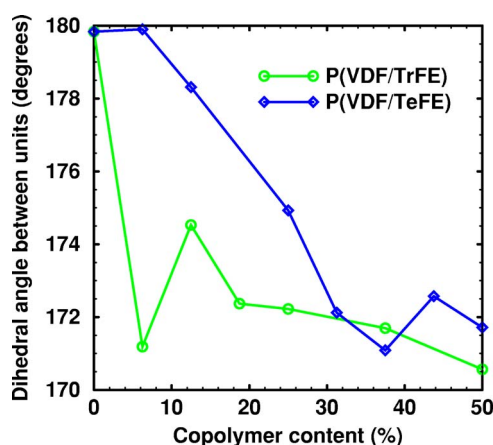


FIG. 8. (Color online) Evolution of the average dihedral angle between monomers in the P(VDF-TrFE) (circles) and P(VDF-TeFE) (diamonds) families with changing copolymer concentration.

dihedral angles of 170° – 172° indicating a less compact monomer arrangement in a chain, i.e., the fluorine atoms “stick out” more. This occurs mostly along the “1” direction, resulting in an increase in a lattice constant.

The observed sensitivity of the dihedral angles in P(VDF-copolymer) mixtures to the presence of asymmetric defects may remove an inconsistency in the conclusions of Hasegawa *et al.*, who obtained better agreement between the measured and the computed structure factors by introducing alternating monomer tilts into their model, but saw no evidence of the appropriate cell-doubling along the backbone direction in their x-ray patterns. It is therefore possible that the actual monomer tilts in their samples were due to the presence of various defects, which would explain the improvement in the structure factor after introducing the tilt. At the same time, the random distribution of defects in a sample explains the absence of the cell-doubling line in the x-ray spectra. In any case, it would be very interesting to refine this experiment using β -PVDF samples produced by modern growth techniques that allow for better control of defect formation and crystallinity.

Turning to the polar properties of P(VDF-copolymer) crystalline models, we computed copolymer concentration-related changes in the dipole moment of every type of monomer (VDF, TrFE, or TeFE) in each model family. The results are shown in Fig. 9, with the limiting values for monomer dipole moments in isolated infinite chains included for comparison. Clearly, the VDF dipole moment decreases in both P(VDF-TrFE) and P(VDF-TeFE) with growing copolymer concentration. However, even at 50-50 VDF-to-copolymer ratio, the VDF unit dipole moments are still approximately 20% larger than those in an isolated β -PVDF chain. The TrFE and TeFE monomer dipole moments in P(VDF-copolymer) crystals demonstrate a strongly nonlinear behavior with respect to copolymer concentration. At TrFE concentration of less than 20%, the TrFE unit in a crystal is more than twice as polar as in an isolated chain. At 50-50 VDF-to-TrFE concentration, it is still 40% more polar than that of an isolated chain. Analogously, in a crystal with TeFE concentration of less than 20%, this naturally nonpolar monomer

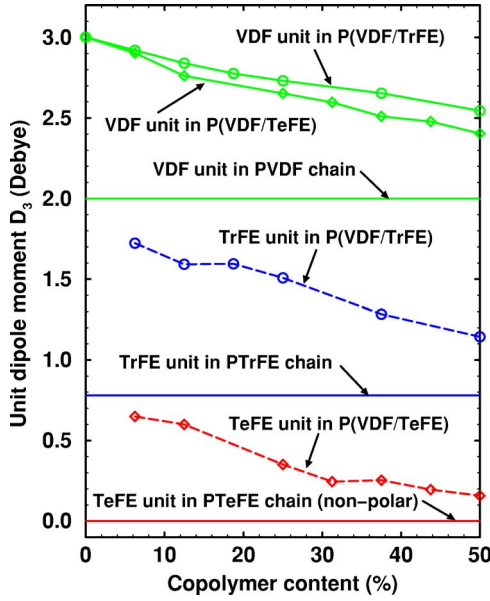


FIG. 9. (Color online) Changes in the values of average dipole moments of VDF, TrFE, and TeFE structural units in the crystalline P(VDF-TrFE) and P(VDF-TeFE) models with increasing copolymer concentration. The limiting values of unit dipole moments in the isolated infinite β -PVDF, PTrFE, and PTeFE chains are shown for comparison.

has a dipole moment of 0.6–0.7 D and it stays polar even at 50-50 VDF-to-TeFE concentration.

Finally, in Fig. 10 we present the copolymer concentration dependence for the total polarization of the crystalline P(VDF-TrFE) and P(VDF-TeFE) models. The curves for both families closely follow the behavior of VDF dipole moments in Fig. 9, displaying a similar downward bowing, which is a bit more pronounced in the case of P(VDF-TeFE). A fit to the curves provides an estimate of polarization (in C/m^2) at any copolymer fraction x in the range between 0 and 0.5:

$$P_3^{\text{TrFE}}(x) = 0.185 - 0.20x + 0.069x^2, \quad (6a)$$

$$P_3^{\text{TeFE}}(x) = 0.185 - 0.34x + 0.201x^2. \quad (6b)$$

A number of experimental observations, representing the polarization extrapolations to perfect crystallinity in β -PVDF, P(VDF-TrFE), and P(VDF-TeFE), are shown in Fig. 10 for comparison. This extrapolation is justified under the assumption that the dipoles in the noncrystalline part are randomly oriented, with zero net polarization. Point (a) refers to the polarization in the β -PVDF film of Ref. 15 linearly extrapolated from 60% crystallinity. The extrapolated value of polarization in the film ($0.167 C/m^2$) is approximately 10% lower than the one obtained in our calculations. Point (b) refers to the 100% polycrystalline 75-25% P(VDF-TrFE) film of Refs. 20 and 21. No correction was made for the variation of polarization direction among the crystalline grains. Point (c) refers to the polarization of 30–85% crystalline samples of 73-27% P(VDF-TrFE) extrapolated to 100% crystallinity by Tajitsu *et al.*,¹⁸ who estimated the

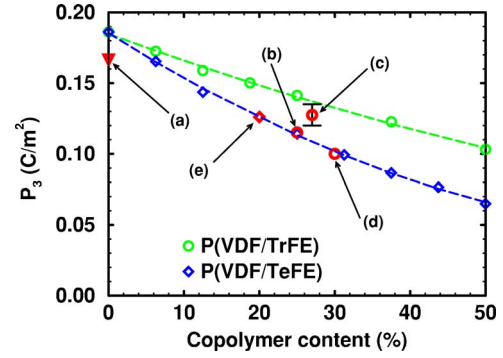


FIG. 10. (Color online) Changes in total polarization in the crystalline P(VDF-TrFE) and P(VDF-TeFE) models with increasing copolymer concentration. The dashed lines represent the fitted curves of Eqs. (6). Extrapolations of experimental polarizations to 100% crystallinity are shown for comparison: (a) β -PVDF film of Ref. 15, (b) polycrystalline 75-25% P(VDF-TrFE) film of Refs. 20 and 21, (c) 73-27% P(VDF-TrFE) sample of Ref. 18, (d) 70-30% P(VDF-TrFE) film of Ref. 41, and (e) 80-20% P(VDF-TeFE) sample of Ref. 19. See text for discussion.

polarization of a fully crystalline sample to be 0.120 – $0.135 C/m^2$. Point (d) refers to a highly crystalline 70-30% P(VDF-TrFE) Langmuir-Blodgett (LB) ultrathin film of Ref. 41. No extrapolation was made here because the crystallinity of the sample is not known. Of these three points, (c) exhibits the best agreement with the calculations. Equation (6a) estimates the polarization in 73-27% P(VDF-TrFE) to be $0.136 C/m^2$, which is almost within the error bar of the experimental extrapolation. Comparing with the points (b) and (d), the computed polarizations are higher by 22% and 30%, respectively. The latter large discrepancy is most probably due to the fact that the 68-nm-thin LB film has not yet reached bulklike polarization. Finally, point (e) refers to the polarization obtained in 43–80% crystalline 80-20% P(VDF-TeFE) samples that were extrapolated to perfect crystallinity in Ref. 19. This point shows an excellent agreement with the calculated polarization. In general, considering that our models represent ideal crystalline systems with no defects and ferroelectric domains, Fig. 10 demonstrates that our computations give an accurate upper-bound estimate of polarization in highly crystalline P(VDF-TrFE) and P(VDF-TeFE) structures through a wide range of copolymer concentrations, and that they can be used as a guide to grow β -PVDF-type crystalline materials with predetermined polar properties.

IV. CONCLUSIONS

We used the Wannier function formalism of the modern theory of polarization to carry out a comprehensive investigation of polar properties of β -PVDF-type chains and crystalline structures. It was explicitly demonstrated that the polarization strengths of VDF and copolymer monomers dramatically depend on their environment. This collective polarization enhancement varies from almost zero in a chain to 50% in a crystal. The latter fact explains why many earlier

models of β -PVDF, which were fitted to a sum of bond-dipole moments of an isolated VDF unit, underestimate the polar properties of bulk polymers. We also studied the effects of weakly polar TrFE and nonpolar TeFE monomers in β -PVDF crystals, mapping out the evolution of the P(VDF-copolymer) structural and polar properties through a wide range of experimentally useful copolymer concentrations. Analogously to β -PVDF, these structures exhibit strong collective polarization enhancement, which has a weakly parabolic dependence on the copolymer concentration.

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