Ab Initio Studies of Polarization and Piezoelectricity in Vinylidene Fluoride and BN-Based Polymers

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Highly piezoelectric and pyroelectric phases of boron-nitrogen-based polymers have been designed from first principles. They offer excellent electrical and structural properties, with up to 100% improvement in the piezoelectic response and an enhanced thermal stability with respect to polyvinylidene fluoride (PVDF). Since methods for their synthesis are readily available, these polymers are extremely promising for numerous technological applications, rivaling the properties of ferroelectric ceramics and superseding PVDF-based materials in high-performance devices.

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Ferroelectric polymers are highly attractive materials for modern technological applications due to their low weight, flexibility, and chemical inertness coupled with substantial piezoelectric and pyroelectric properties [1–5]. Furthermore, their low acoustic impedance matches well with water and organic tissue. Such a fortunate combination of properties allows for a wide employment of ferroelectric polymers in modern industry, with applications ranging from various sensors, actuators, and transducers to ferroelectric optical memory, sonar equipment, and artificial muscles. Still, polarization and piezoelectricity in ferroelectric polymers are about an order of magnitude weaker than in perovskite ferroelectrics, such as lead zirconate titanate [6,7]. On the other hand, perovskite ferroelectrics are usually heavy, brittle, and toxic, which limits their technological usefulness. In this Letter, we combine simple "bond-dipole" arguments with rigorous *ab initio* calculations to predict and assess the properties of novel "superpolar" polymeric structures, obtained by substitution of the carbon backbone with boron and nitrogen. The substitution leads to a 100% improvement in piezoelectric response and thermal stability over ordinary ferroelectric polymers, while retaining their excellent mechanical and environmental properties.

The most well known and widely used family of ferroelectric polymers includes polyvinylidene fluoride (PVDF), $[–CH_2–CF_2–]_n$, and its copolymers with trifluoroethylene (TrFE), $[–CHF–CF_2–]$, and tetrafluoroethylene (TeFE), $[–CF_2–CF_2–]$. In its most polar β phase, PVDF, which can be grown 50% crystalline, has spontaneous polarization of 0.05–0.08 C/m^2 and piezoelectric stress constants of up to 0.1 C/m^2. The nature of polarization in β-PVDF can be qualitatively understood from a simple bond-dipole picture, shown in Fig. 1(a). The dipole moments of the two F-C and two C-H bonds add up in such a way that the $[–CH_2–CF_2–]$ monomer gets an effective dipole moment in the direction perpendicular to the carbon backbone. The "bottom" fluorine part of the monomer becomes negative and the "top" hydrogen part positive. The TrFE and TeFE monomers [see Fig. 1(b)] in PVDF copolymers, which are structurally similar to β-PVDF, are less polar than VDF, which is easily explained in the same bond-dipole picture. When one or both H atoms at the top of the monomer are substituted by fluorines, the dipole moments of the new F-C bonds partially or completely cancel the moments of the two F-C bonds at the bottom. Still, the polar properties of PVDF copolymers are often as good as or even better than those of "pure" β-PVDF, because they can be grown up to 80%–90% crystalline [2].

The simple bond-dipole view on polarization, coupled with the electronegativity argument of Pauling [8], not only gives a qualitative explanation of the properties of such polar materials, but also provides clues to how these properties could be enhanced. In the case of β-PVDF, the fluorine end of the VDF monomer can be made even more negative if carbon in the F-C bonds is replaced by a less electronegative atom. In the same fashion, the hydrogen end of the monomer becomes more positive with a more electronegative atom substituting for carbon in the C-H bonds. For example, if we replace C atoms with B at the bottom and N at the top, the polarity of both F-B and N-H bonds is greatly magnified, thus making the effective monomer dipole moment larger than in VDF. The resulting $[–BF_2–NH_2–]_n$ polymer is called polyaminodifluoroborane (PADFB). Furthermore, the ordered phase of $[–BH_2–NH_2–]_n$ or polyaminoborane (PAB), the BN analog of polyethylene, $[–CH_2–CH_2–]_n$, must also be piezoelectric and pyroelectric by virtue of the strong polar nature of the N-H bonds. The monomers of both of these structures are shown in Fig. 1(c).

Although the bond-dipole model provides some important hints about the properties of polar materials and how they can be improved, it cannot precisely assess the *magnitude* of this improvement or evaluate whether the

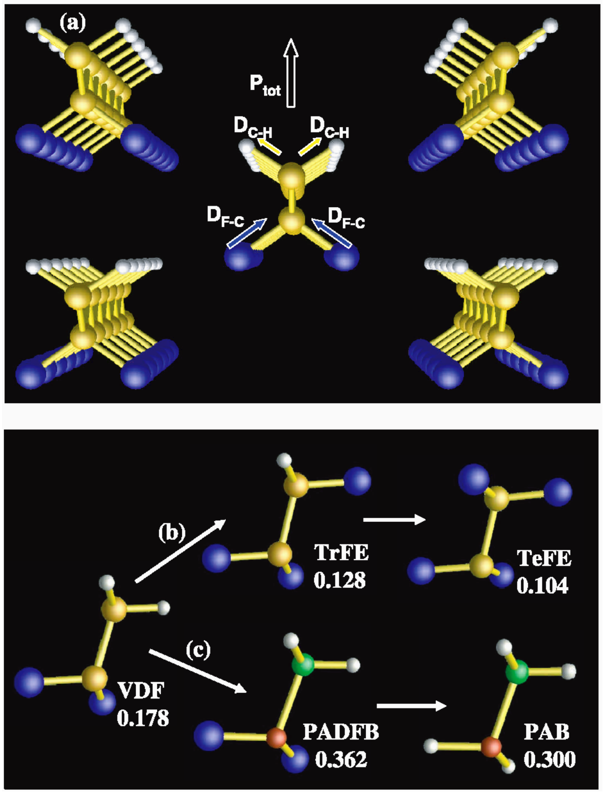

FIG. 1 (color online). Polarization in β-PVDF and related polymers. (a) The structure of the crystalline β phase of PVDF. The polar-covalent nature of the F-C and C-H bonds leads to polarization in the VDF monomer, directed perpendicular to the carbon backbone. $\boldsymbol{D}_{\text{F-C}}$ and $\boldsymbol{D}_{\text{C-H}}$ are the bond-dipole moments. The second panel illustrates the evolution of the VDF monomer into TrFE and TeFE by substitution of the H atoms with F atoms [pathway (b)], and into PADFB and PAB by substitution of the carbon backbone with borons and nitrogens [pathway (c)]. Spontaneous polarization (in the units of C/m^2) is given for each polymer.

improved material would be stable. The results produced by a number of bond-dipole-based empirical models for β-PVDF [9–14] vary considerably depending on the particular choice of dipole-dipole interaction and specific values assigned to "monomer dipoles" (see Table I). Moreover, direct comparison to experiments is dubious here, because of the low crystallinity of experimental samples of β-PVDF.

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

Model	Year	C (%)	P^{sp} (C/m^2)	Ref.
Rigid dipoles		100	0.131	[3]
Kakutani-Mopsik *et al.*	1970–1975	100	0.22	[9,10]
Tashiro *et al.*	1980	100	0.140	[11]
Purvis-Taylor	1982–1983	100	0.086	[12]
Al-Jishi–Taylor	1985	100	0.127	[13]
Carbeck *et al.*	1995	100	0.182	[14]
Real material		≈ 50	0.05–0.08	

A different approach should be applied to compute polar properties of materials that *does not* partition them into a collection of dipoles and has all the multipole interactions naturally "built in." In this Letter we employ the modern theory of polarization to compute polarization from first principles. The numerical accuracy and predictive power of this approach allow us to make *quantitative* assertions about the improvement in the polar properties of these new materials. An additional benefit of this technique is that our results for β-PVDF, where comparison with the experiment cannot be easily made, can serve as a reference for "calibration" of the empirical models.

We used an *ab initio* multigrid-based total-energy method, employing a real-space grid as a basis [15] for all the calculations presented here. The exchange-correlation interaction was described by the generalized gradient approximation of Ref. [16]. The norm-conserving pseudopotentials [17,18] were generated by the FHI98PP package [19]. Polarization was computed by using the "Berry-phase" technique [20] where the polarization difference between two states of a system $\Delta\boldsymbol{P} = \boldsymbol{P}^{(\lambda_1)} - \boldsymbol{P}^{(\lambda_0)}$ can be obtained as a geometrical quantum phase, if an adiabatic transformation pathway λ from one state to the other exists and leaves the system insulating. In this method the polarization can be written as a sum of ionic and electronic contributions:

$$\begin{aligned}\boldsymbol{P}^{(\lambda)} &= \boldsymbol{P}^{(\lambda)}_{\text{ion}} + \boldsymbol{P}^{(\lambda)}_{\text{el}} \\ &= \frac{e}{V}\sum_{\tau} Z^{(\lambda)}_{\tau}\boldsymbol{r}^{(\lambda)}_{\tau} - \frac{2ie}{8\pi^3}\sum_{i\,\text{occ}}\int_{BZ} d\boldsymbol{k}\langle u^{(\lambda)}_{ik}|\nabla_{\boldsymbol{k}}|u^{(\lambda)}_{ik}\rangle,\end{aligned} \tag{1}$$

where V is the volume of the unit cell, Z_τ and $\boldsymbol{r}_\tau$ are the charge and position of the τth atom in the cell, and u_{ik} are the occupied cell-periodic Bloch states of the system. The value of $\boldsymbol{P}^{(\lambda)}$ can be obtained by computing the total geometrical phase

$$\Phi^{(\lambda)}_{\alpha} = \sum_{\tau} Z^{(\lambda)}_{\tau}\boldsymbol{G}_{\alpha}\cdot\boldsymbol{r}^{(\lambda)}_{\tau} + V\boldsymbol{G}_{\alpha}\cdot\boldsymbol{P}^{(\lambda)}_{\text{el}}/e, \tag{2}$$

defined modulo 2π. Here $\boldsymbol{G}_\alpha$ is the reciprocal lattice vector in the direction α along which we would like to compute polarization. The first "ionic" term in Eq. (2) is nothing but a simple lattice summation, while the second "electronic" term (Berry phase) is computed from first principles. The total polarization of the system is then recovered as follows:

$$\boldsymbol{P}^{(\lambda)}_{\alpha} = e\Phi^{(\lambda)}_{\alpha}\boldsymbol{R}_{\alpha}/V, \tag{3}$$

where $\boldsymbol{R}_\alpha$ is the real-space lattice vector corresponding to $\boldsymbol{G}_\alpha$, $(\boldsymbol{R}_\alpha\cdot\boldsymbol{G}_\alpha) = 1$.

Spontaneous polarization calculations with the Berry-phase method require a nonpolar reference configuration to obtain the difference $\Delta\boldsymbol{P}$. We chose as such a reference the system where one of the polymer chains in the cell is rotated 180° around its backbone direction, so that the effective dipole moments of the two chains are antiparallel.

Piezoelectric properties of polymers, which are directly related to the change of their polarization due to strain, were also computed with the Berry-phase technique. In the linear regime, such a polarization change in the system along the polar (z) axis is

$$\delta P_3 = e_{31}\epsilon_1 + e_{32}\epsilon_2 + e_{33}\epsilon_3, \qquad (4)$$

where $e_{3\alpha}$ are the piezoelectric stress constants, $\epsilon_1 = (a - a_0)/a_0$, $\epsilon_2 = (c - c_0)/c_0$ and $\epsilon_3 = (b - b_0)/b_0$ are the strains along the x, y, and z axes, and a_0, b_0, and c_0 are the equilibrium values of the lattice parameters. The piezoelectric constants $e_{3\alpha}$ are obtained as $[P_3^{(1)} - P_3^{(0)}]/\epsilon_\alpha$, where $P_3^{(1)}$ and $P_3^{(0)}$ are the values of polarization in the strained and unstrained versions of the system.

The calculations for β-PVDF were performed using an orthorhombic periodically repeated cell, containing four VDF monomers arranged into two chains in all-*trans* conformations. A 75/25 mol % model of the P(VDF/TrFE) copolymer was constructed by substituting a H atom by a F atom in one of the four VDF monomers in the cell. The corresponding change for the second H atom *in the same monomer* produced a 75/25 mol % model of the P(VDF/TeFE) copolymer [see Fig. 1(b)]. In both models the mol % ratio of the VDF content to the copolymer is approximately the same as in many experimentally grown samples of P(VDF/TrFE) and P(VDF/TeFE) with large polar properties [2,21–24]. All copolymer models were volume optimized, which resulted in slightly larger cells than for the β-PVDF model.

Our results for the spontaneous polarization and piezoelectricity in PVDF and its copolymers are presented in Table II. For β-PVDF we find a significant polarizing effect due to dipole-dipole interaction (0.178 vs 0.131 C/m^2 in the rigid-dipoles model [3]). For the copolymers the polarization becomes smaller as we go from pure PVDF to P(VDF/TrFE) and then to P(VDF/TeFE), just as the bond-dipole picture suggests. As no rigorous comparison between the experimental and theoretical data is possible for β-PVDF, some authors [3,5,13] simply divide their polarization values by two, which only crudely indicates a possible agreement between the experiment and a given theoretical model. For the copolymers, on the other hand, the situation is less uncertain because in the range of 50%–80 mol % VDF they can be grown up to 80%–90% crystalline [2]. An accurate polarization extrapolation to 100% crystallinity for the P(VDF/TeFE) copolymer was made in Ref. [22], and our calculation is in excellent agreement with this result. An analogous extrapolation for the P(VDF/TrFE) copolymer in Ref. [21] (see also Ref. [2]) is again very close to the result of our calculations. The only experimentally measured piezoelectric stress constants for 100% crystallized P(VDF/TrFE) are given in Ref. [23]. Unfortunately, this material is polycrystalline and the values of the single crystalline piezoelectric constants cannot be extracted from these results.

We computed the spontaneous polarization and piezoelectric response in the PADFB and PAB polymers, using the same approach as for β-PVDF. Both structures were volume optimized, which resulted in smaller unit cells compared to β-PVDF. Lattice parameters, spontaneous polarization, and piezoelectric constants for the BN-based polymers are given in Table III. Similar data for β-PVDF and $PbTiO_3$ are also included. For PADFB the polarization is raised by 100%, compared to β-PVDF, which leads to nearly twofold enhancement of the piezoelectric properties. For PAB we see a 50% increase in spontaneous polarization accompanied by a 30%–40% improvement in the piezoelectric constants. We also computed the chain-rotation barriers in the BN-based polymers, shown in Fig. 2, to estimate the stability of the polar phase in these materials. The peaks around 60° and 150° in the energy curves for β-PVDF and PADFB correspond to the positions where the F atoms in the rotated and fixed chains come close to each other. The curve for PAB, which does not contain fluorines, lacks these features, making this polymer significantly less stable than β-PVDF with a low chain-rotation barrier of 0.28 eV per monomer. The height of the barrier in PADFB is about 2.4 eV per monomer, more than 3 times larger than in β-PVDF (0.72 eV), showing that the polar phase in PADFB should be much more stable than in β-PVDF.

TABLE II. Polarization and piezoelectric constants (all in the units of C/m^2) for PVDF and its copolymers.

	P_3^{sp}	e_{31}	e_{32}	e_{33}	Ref.
PVDF	0.178	−0.268	−0.270	−0.332	
		−0.130	−0.145	−0.276	[11][a]
	0.182	−0.26	−0.09	−0.25	[14][a]
P(VDF/TrFE) (75/25)	0.128	−0.183	−0.192	−0.211	
	0.123				[2,21][b]
P(VDF/TeFE) (75/25)	0.104	−0.135	−0.145	−0.150	
	0.118				[22][b]

[a] Computation.

[b] Experimental result extrapolated to 100% crystallinity and rescaled for the 75/25 mol % content.

TABLE III. Polar properties of the BN-based polymers, compared to β-PVDF and $PbTiO_3$. Lattice parameters a, b, c are given in Å, spontaneous polarization P_3^{sp} and piezoelectric constants $e_{3\alpha}$ in C/m^2.

	a	b	c	P_3^{sp}	e_{31}	e_{32}	e_{33}
β-PVDF	8.58	4.91	5.12	0.178	−0.268	−0.270	−0.332
PADFB	8.18	4.62	5.33	0.362	−0.493	−0.580	−0.555
PAB	7.60	4.49	5.21	0.300	−0.348	−0.398	−0.431
$PbTiO_3$[a]				0.88	−0.93		3.23

[a] Reference [7]. Tetragonal configuration with a polar (001) axis.

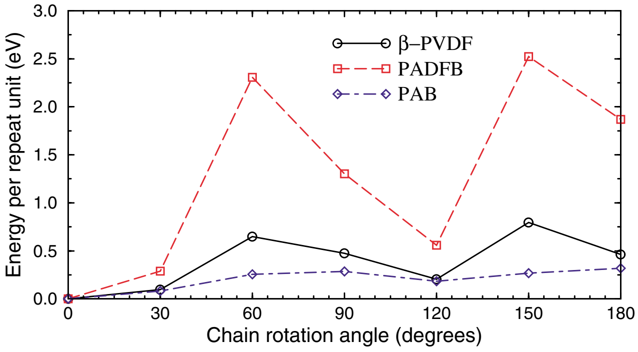

FIG. 2 (color online). Total energy calculations for rotating chains in β-PVDF and BN-based polymers. The energy barriers for these rotations determine the thermal stability of polymers. See the text.

The last result is consistent with the experimental evidence [25] of increased thermal stability of PADFB.

Both of the BN-based polymers, for which we show that their ordered phases are highly polar, are already well known. PAB, for example, is routinely used as a precursor for preparing h-BN [25,26]. PADFB has also been synthesized, although not yet in large quantities. However, several authors indicate that developing such a process is relatively straightforward [25,27]. In analogy with PVDF, where the polar polymers are *manufactured* from initially nonpolar films by stretching and poling [1,3,5], we expect that similar postprocessing techniques will be needed to make oriented BN films. The magnitude of the polarization will obviously depend on the degree of alignment, with our results for an all-*trans* configuration being the upper limit.

In summary, combining a simple bond-dipole picture of polarization with precise *ab initio* calculations, we propose an atomic-substitution procedure for improving the properties of polar materials. Applied to β-PVDF, this procedure produces highly polar phases for polyaminoborane and polyaminodifluoroborane polymers. We predict an up to 100% enhancement of the spontaneous polarization and piezoelectric response for these BN-based structures, when compared to β-PVDF. Such materials, combining improved polar properties—comparable to those of the ferroelectric ceramics—with excellent mechanical and environmental properties, inherited from PVDF, could dramatically expand the scope of applications of ferroelectric polymers in modern industry.

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