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ABSTRACT

Using first-principles simulations, we identify the microscopic origin of the non-linear dielectric response and high energy density of PVDF-based polymers as a cooperative transition path that connects non-polar and polar phases of the system. This path explores a complex torsional and rotational manifold and is thermodynamically and kinetically accessible at relatively low temperatures. Furthermore, the introduction of suitable copolymers significantly alters the energy barriers between phases providing tunability of both the energy density and the critical fields.

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The usual means of storing electrical energy are either *batteries*, where the current induces chemical reactions, or *capacitors*, where especially chosen *dielectrics* enhance the stored energy. Current batteries offer *energy densities* of about 10^2-10^3 Wh/kg, but their *power densities*, *i.e.*, the speeds at which they can be discharged, are only 50-300 W/kg [1]. Fuel cells have energy densities [1] several times larger than batteries, but their power densities are significantly lower. Conventional capacitors have energy densities of only ~ 0.05 Wh/kg, but their power densities reach 10^5 W/kg and they can be fully discharged over 10^6 times, compared to 200-1000 times for batteries. They can thus be used to release or store quick bursts of energy, *e.g.*, in acceleration or regenerative breaking. Ultracapacitors, or electric double-layer capacitors, occupy a middle ground in energy storage. They achieve energy densities of ~10 Wh/kg and power densities of ~10^3 W/kg [1] by using porous plates suspended in an electrolyte to attract negative/positive ions to the positive/negative electrodes, thereby dramatically shrinking the distance between the positive and negative "layers." This increases the capacitance per unit area, $c = \varepsilon_0 K/d$, where K is the dielectric permittivity and d is the distance between capacitor plates. However, the charge/discharge speeds of ultracapacitors are limited by ion diffusion in the electrolyte, while the porosity of the plates leads to small breakdown voltages within each cell. In contrast, by using ultrafast phase transitions as the primary mechanism of energy storage, PVDF-based capacitors reach the power densities and breakdown fields of conventional capacitors, while their energy densities are 10^2-10^3 larger, potentially rivalling those of ultracapacitors.

In traditional capacitors, the stored energy density is given by $U = 1/2\ \varepsilon_0 K(E_b)^2$, where E_b is the electric breakdown field. Enhancement of K and/or E_b leads to increased energy storage. However, both are native properties that are constants for any chosen material. High K materials such as ferroelectric oxides have low E_b. Polymers typically have high E_b but very small K. Materials that have both high K and high E_b have not yet been found and attempts to create composites with the same characteristics have not yet

met with success. An alternative avenue to enhance the stored energy is to search beyond "linear" dielectrics for materials where the effective K changes with the applied field. This Letter describes the mechanism by which concerted atomic transformations induced by the electric field lead to phase transformations in polyvinylidene fluoride (PVDF: $(C_2H_2F_2)_n$) based polymers, resulting in storage densities rivalling those of ultracapacitors while maintaining the power densities associated with traditional capacitors. The phase-transition route could also be explored in other systems that undergo field-induced structural transformations, providing a different, largely unexplored route for optimizing materials with high power and storage densities.

Chu *et al.* [2] have shown that an admixture of 9% CTFE (chlorotrifluoroethylene: CF_2CClF) impurities into PVDF results in an order of magnitude increase in energy density, reaching 17 J/cm^3. The dramatic non-linear dependence of energy density on CTFE concentration is a clear indication that a structural change must be involved. Indeed, we have previously postulated [3] that the greatly enhanced energy density is due to a reversible phase transition induced by the electric field. This assertion is supported by the fact that the non-polar state is observed as the initial phase in x-ray spectra [2]. However, the atomistic mechanism of the transformation was not determined and previous work suggested that kinetic barriers for polymer transformations are ~1 eV [4], precluding the fast kinetics observed experimentally. In contrast, the studies of multistage *concerted* motion described below uncover a novel mechanism in the PVDF family of polymers with modest energy barriers, easily capable of transforming their structure at room temperature. Furthermore, these barriers can be significantly modified by admixing appropriate copolymers, which provide a novel avenue for optimizing the properties of energy-storage materials for specific applications.

The structure of a single PVDF polymer chain is characterized by dihedral angles between the individual monomers: when the dihedral angles alternate between -57° and +57° the chain is in a trans-gauche conformation (TGTG'), see Fig. 1(a), while when all the dihedrals are equal to 180°, the chain is in an all-trans conformation (TT). As the individual chains organize in a crystalline environment, they can form four different polymorphs, depending on the individual conformations of the chains and their relative orientation: (i) anti-polar TGTG' (α-PVDF), (ii) polar TGTG' (γ-PVDF) with polarization of 0.09 C/m^2 per unit cell, (iii) anti-polar TT (δ-PVDF), and (iv) polar TT (β-PVDF), with polarization of 0.19 C/m^2 per unit cell. The structural and energetic data for these structures are provided in the supplementary material.

In our previous work [3], we have shown that the thermodynamically preferred phase of P(VDF-CTFE) with a low CTFE concentration changes from the non-polar α to the polar β phase as the electric field increases. However, a direct transformation from α- to β-PVDF, although thermodynamically feasible, would require unphysically large electric fields. Only by assuming a disordered multi-domain structure with a distribution of concentrations, the gradual non-linear dielectric response seen in experiments becomes reproducible. This assumption, albeit successful in interpreting the experimental data, falls short of providing a satisfactory microscopic explanation of the mechanism of high energy density storage in PVDF and its copolymers. Motivated by an early experiment [5] where it was postulated that α and β chains of PVDF are related to each other by rotational transformations, our current work probes the non-polar to polar phase transition as a sequence of non-trivial but nevertheless easily characterized symmetry operations: (i) in the rotational manifold of α-PVDF, rotating one of the polymer chains by 180° yields γ-PVDF, and (ii) β-PVDF is a torsional manifold of γ-PVDF. A clear topological pathway is thus available to the system to morph from one phase to the other, first by transforming from the anti-polar α phase to

the polar γ phase (Fig. 1(c)), and then changing all of the dihedral angles from ±57° to 180° and reaching the β phase (Fig. 1(d)). As a consequence, PVDF can exhibit an adaptable response to electric fields by selecting an appropriate functional structure chosen from its large ensemble of interrelated topological states. However, this manifold of torsions and interchain rotations must be thermodynamically and kinetically accessible at relatively low temperatures for the transformations to occur. If a low-barrier transition path exists, it would lead to non-linear dielectric response and could consequently explain the high energy density observed in *some* PVDF-based materials.

We evaluate the energies of the intermediate structures along the α→γ→β pathway shown in Fig. 1 for both PVDF and P(VDF-CTFE) 90/10 mol%, using first-principles calculations based on density-functional theory. Total energy calculations are performed using density-functional theory (DFT) [6, 7] with Vanderbilt ultrasoft pseudopotentials [8] and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [9], as implemented in the quantum-ESPRESSO package [10]. We choose a cut-off energy of 35 Rydberg. A Monkhorst-Pack [11] **k**-point grid of 2x4x4 gives well converged results for α, γ, and β unit cell structures. In the relaxation process the forces are converged to less than 0.05 eV/Å and stresses to less than 0.05 GPa. The Berry phase approach used to calculate polarization is described in Ref. [12]. For total energy calculation we relax the cell volume and atomic coordinates while keeping the dihedral and interchain angles constrained to the chosen values. The interchain interactions in polar polymers are dominated by electrostatics, which makes the PBE functional suitable for our studies, but we have also evaluated the contribution of van der Waals interactions to the ground state energies of the α, γ, and β phases using the semi-empirical DFT-D [13] implementation within PWSCF. The dispersion energies are almost the same and hence cancel out in the total energy differences. Since we are interested in total energy differences, we perform other calculations without the dispersion energy. The unit cell contains 24 atoms for pure PVDF. There are two

chains, each with two VDF monomers, in the unit cell. The unit cell for PVDF-CTFE (10% CTFE) has 120 atoms with two parallel chains. There are 9 VDF monomers and one CTFE monomer in each chain. The total energy difference is divided by the total number of carbon atoms to compare the results of PVDF with those of PVDF-CTFE. The structural parameters, total energy differences between the phases and atomic coordinates are provided in the supplementary material.

In order to reach the minimum energy structures, we perform atomic and volume relaxations at all intermediate points along the path. Starting from the α structure, we gradually rotate one of the chains to sample the potential energy surface associated with the rotational manifold connecting the α and γ structures (see Fig. 1(c)). The transition from γ to β, depicted in Fig. 1(d), involves a TGTG' to an all-trans (TT) transformation. We generate intermediate structures by alternatively changing the dihedral angles in steps of ±Δθ (Δθ = 15°) from their values in the γ configuration (±57°) to the final β geometry (180°). The intermediate structures thus created are fully relaxed, under the constraint that the dihedral angles remain at their assigned values. The unit cell volume is also continuously optimized during the transformation. In Fig. 2(a) we display the values of the total energy per C atom along the transformation pathway as a function of the two independent principal order parameters: the interchain angle (θ) and the dihedral angle (φ). First, θ changes from 0° to 180° and then φ changes from ±57° to 180° while holding θ=180°. Our results demonstrate the existence of a low barrier energy path, starting from the stable non-polar native α phase to the polar higher-energy β phase with a relative energy difference of ~24 meV/C-atom. The intermediate polar γ phase is metastable, with an energy 32 meV/C-atom greater than the α phase.

The energy barriers for the α➔γ and the γ➔β transitions are 50 and 100 meV/C-atom, respectively. In the same figure we also report results for the P(VDF-CTFE) 90/10 mol% case. The introduction of CTFE has a dramatic effect on the kinetics of the

transformation. The energy barrier between α and γ is now reduced by almost a factor of 2 to less than 25 meV/C-atom, and the one between γ and β to less than 60 meV/C-atom. This drastic reduction in activation energies makes the phase transformation kinetically accessible at considerably lower temperatures and it dramatically lowers the critical electric field that will trigger the transformation.

It is important to note that the mechanism for the transformation that we propose involves a concerted rotation of the whole polymer chain for the α➔γ transition, and a collective change of all the dihedral angles in the γ➔β transition. While the α➔γ transformation involves only a topologically trivial operation, the actual phase transition path from γ to β has been a matter of speculation. All models that have been considered to date imply a mechanism based on the nucleation of a single dihedral angle mutation, such as …(TGTG')-(T**G**TG')-(TGTG')…➔…(TGTG')-(T**T**TG')-(TGTG')… in an otherwise unchanged monomer sequence (the so called kink nucleation) [4]. The calculated barrier for the formation of a kink, ~1 eV/C-atom [4], is however much higher than the 100 meV barrier for the cooperative, concerted rotation described above. Clearly, only the cooperative transition is fast enough to account for the experimental observations.

The phase transition occurs when an electric field E is applied and the system minimizes the electric field enthalpy $F = E - V \boldsymbol{P} \cdot \boldsymbol{E}$, where E is the internal energy and P is the polarization. For the fully relaxed polar γ and β phases of PVDF and PVDF-CTFE phases, we calculate the polarization using the first-principles Berry phase approach [12]. For the intermediate stages along the transition path, the cooperativity of the phase transformation mechanism allows as to introduce a simple geometrical model for the total electric polarization of the system as a vector sum of rigid dipoles belonging to single monomers. As the rotational or dihedral angle changes, the value of the vector sum also changes according to the analytical expression:

$$P = d[1 + \cos(\phi + 180°)] + 4d \cos(57° - \theta) \tag{1}$$

where d (~0.05 C/m^2) is the rigid dipole of a single VDF monomer, extracted from the β-structure Berry-phase calculation. Although this model leaves out small nonlinear effects due to interchain interactions [14] it is still surprisingly accurate, as evidenced by comparisons to Berry phase calculations for the γ structure. The calculated polarization along the α→γ→β transition path is plotted in Fig 2(b), together with the Berry phase values. The figure shows that polarization is only weakly affected by the 10% admixture of CTFE. Its large value leads to significant lowering of the enthalpy barriers separating the three phases. Fig. 2(c) displays the electric enthalpy at different values of the electric field. At 500 MV/m, the activation enthalpies for α→γ and the γ→β transitions become 32 and 88 meV/C-atom, respectively, for pure PVDF, and 18 and 50 meV/C-atom for P(VDF-CTFE) 90/10 mol%. As expected from the $V \, \boldsymbol{P} \bullet \boldsymbol{E}$ term, for the highest values of the electric field the electric enthalpy of the β phase drops below that of α. Fig. 2(c) clearly shows that a strong electric field both enables and accelerates the transformation to the β phase. Furthermore, the introduction of a small amount of CFTE has a dramatic effect on the transformation, because the polarization along the transition path does not change significantly, but the enthalpy barriers are reduced considerably. The combination of these two effects greatly enhances the kinetics and enables a fast response even at moderate temperatures.

The original evidence for structural transition under electric field came from Ref. [2]. The films of PVDF-CTFE were annealed at 120° C for 14 hours to improve crystallinity. X-ray data for stretched and unstretched PVDF-CTFE were compared to those of pure PVDF. It was found that both unstretched and stretched PVDF-CTFE were mostly in the non-polar α phase at zero electric field, Under electric field a transition to the polar β phase was observed as evidenced by enhanced electric displacement under electric field. Furthermore, evidence for the presence of all three

phases was presented by Guan et al. [15] based on wide-angle X-ray diffraction and Fourier transform infrared spectroscopy experiments. Although the structural transformation pathway proposed by us has not yet been observed, the low transition barriers calculated above make it a strong candidate for explaining the fast charge-discharge cycles observed experimentally [2].

The identified pathway with its low activation barriers already proves the feasibility of the field-induced $\alpha \rightarrow \beta$ transformation. Due to computational constraints we have not investigated simultaneous changes in both order parameters, which could result in even lower activation energies. Furthermore, our investigations focused on crystalline materials, while the morphology of as-grown PVDF and its copolymers is quite complicated, usually resulting in multi-domain spherulites [16]. In fact, the multi-domain structure should facilitate the transformation by providing environments with varying CTFE concentrations and geometries. Since changes in volume are involved, the transitions are *first-order* and their nucleation should be enhanced by the presence of defects. Nevertheless, the calculated barriers are still high enough that the phase transitions are thermally activated. In addition, the presence of domain boundaries, defects and/or mobile charges will enhance the stabilities of particular phases, leading to hysteresis and hence loss, as experimentally observed.

In summary, we have uncovered the mechanism behind the non-linear dielectric response of certain PVDF-based polymers and showed how it can lead to ultrafast energy discharge *and* high energy density. This combination of properties is due to electric-field-induced phase transition from a ground state nonpolar structure to a higher-energy polar structure. We showed that the relevant order parameters for the transition are collective changes of rotational and dihedral angles, rather than the formation and propagation of localized kinks. We also demonstrated that an addition of a small amount of a copolymer results in: (i) a significant reduction of energy barriers,

and (ii) a small change in polarization. The combination of (i) and (ii) leads to dramatic reductions of the electric enthalpy barriers along the transition path. Finally, we believe that copolymers can also be chosen with the goal of controlling the morphology and microstructure as well as optimizing the energy hypersurface, in order to minimize hysteresis and loss.

[1]   P. F. Flynn, *Meeting the Energy Needs of Future Warriors* (National Academies Press, Washington D.C., 2004).

[2]   B. Chu, X. Zhou, K. Ren, B. Neese, M. Lin, Q. Wang, F. Bauer, and Q. M. Zhang, Science **313**, 334 (2006).

[3]   V. Ranjan, L. Yu, M. Buongiorno-Nardelli, and J. Bernholc, Phys. Rev. Lett. **99**, 047801 (2007).

[4]   H. Su, A. Strachan, and W. A. Goddard III, Phys. Rev. B **70**, 064101 (2004).

[5]   G. T. Davis, J. E. McKinney, M. H. Broadhurst, and S. C. Roth, J. Appl. Phys. **49**, 4998 (1978).

[6]   P. Hohenberg, and W. Kohn, Phys. Rev. **136**, B864 (1964).

[7]   W. Kohn, and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[8]   D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).

[9]   J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[10]   P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L.

Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, and R. M. Wentzcovitch, J. Phys. Condens. Matter **21**, 395502 (2009).

[11]   H. J. Monkhorst, and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

[12]   D. Vanderbilt, and R. D. King-Smith, Phys. Rev. B **47**, 1651 (1993).

[13]   S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. **132**, 154104 (2010).

[14]   S. M. Nakhmanson, M. Buongiorno-Nardelli, and J. Bernholc, Phys. Rev. B **72**, 115210 (2005).

[15]   F. Guan, J. Wang, J. Pan, Q. Wang, and L. Zhu, Macromolecules **43**, 6739 (2010).

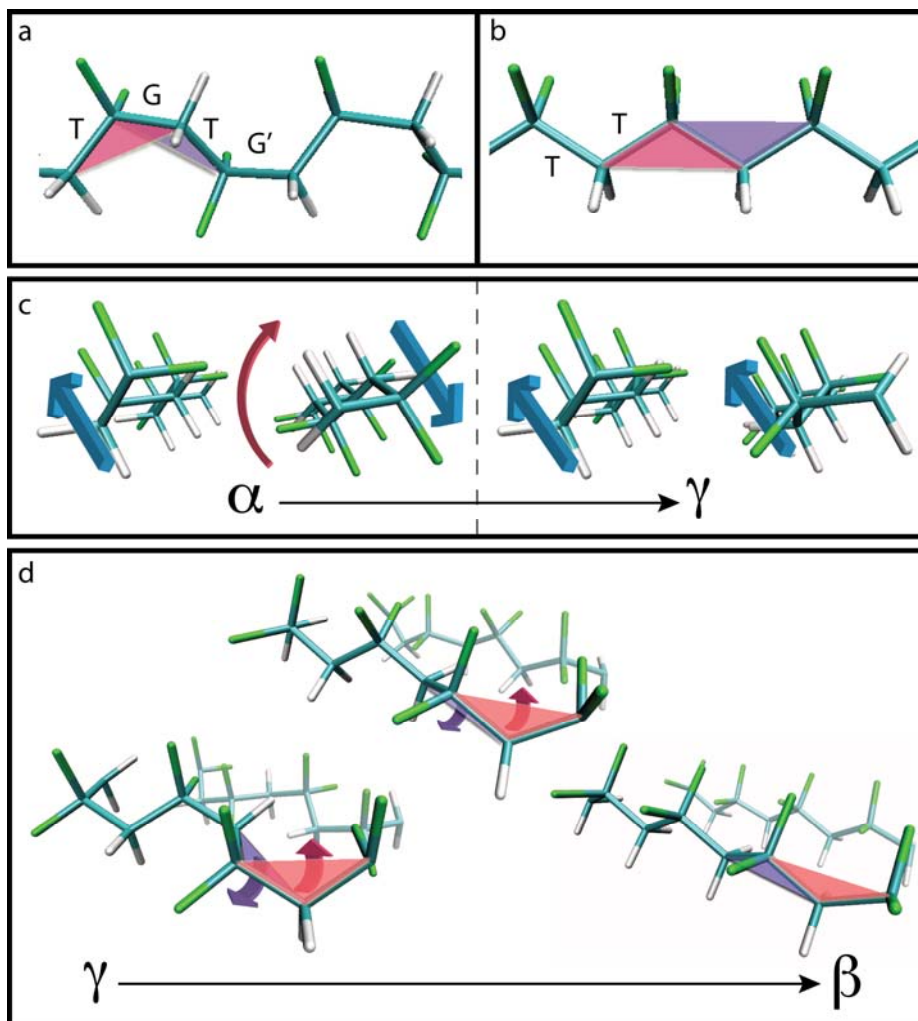[16]   A. J. Lovinger, Science **220**, 1115 (1983).

Figure 1

Conformations and transition pathways in PVDF: (a) Trans-gauche configuration (TGTG'), in which the dihedral angles alternate between trans (180°) and gauche (±57°); (b) All-trans geometry (TT) where all the dihedral angles are 180°; (c) Starting from the anti-polar α phase one can rotate one of the chains about its axis by 180°, to align the dipoles and create the polar γ phase; (d) Transformation from the γ to the β phase is achieved by gradually changing the dihedral angles in each chain from ±57° to 180°.
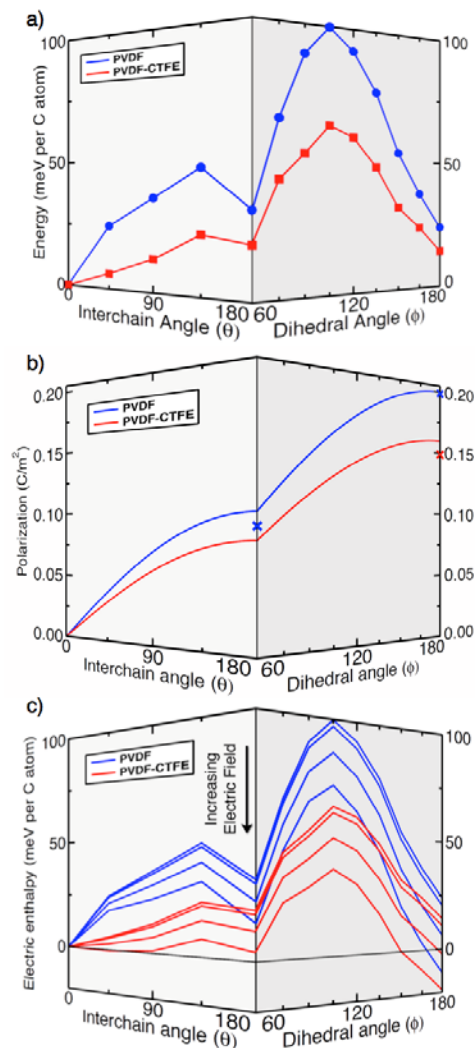
Figure 2

Energetics and polarization along the transformation pathway from the α to the β phase, for pure PVDF and P(VDF-CTFE) 90/10 mol%. The change in interchain angle from 0° to 180° results in the α→γ transition, while the change in the dihedral angle from ±57° to 180° describes the γ→β transformation: (a) total energies, and (b) polarizations from eq. (1). In (b) crosses display polarization values calculated using the first-principles Berry-phase approach. (c) Electric enthalpies for electric fields of 0, 100, 500 and 1000 MV/m as functions of the order parameters.