

Large electrostrictive strain at gigahertz frequencies in a polymer nanoactuator: Computational device design

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Using molecular dynamics with a first-principles-based force field (denoted MSXX), we show that large electrostrictive strains ($\sim 5\%$) at extremely high frequencies (over $\sim 10^9$ Hz) can be achieved in a poly(vinylidene-fluoride) nanoactuator if the packing density of the polymer chains is chosen appropriately. We control the packing density by assembling the polymer chains on a silicon $\langle 111 \rangle$ surface with one-half coverage. Under these conditions, the equilibrium, zero electric field conformation of the polymer contains a combination of gauche and trans bonds. This structure can be transformed to an all- T conformation by applying an external electric field. Such molecular transformation is accompanied by a large deformation in the direction of the polymer chains. The device shows typical electrostrictive behavior with strain proportional to the square of the polarization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1862343]

Materials that interconvert mechanical and electrical energy have received significant attention due to their important technological applications as actuators, sensors and transducers in a wide range of devices, such as artificial muscles, pumps, and noise reduction systems. Desired design properties include: High strain, speed, and precision, as well as good energy density and conversion factor. Within this class of materials, electroactive polymers have recently attracted large interest due to a variety of unique properties, such as good acoustic matching with biological materials and water, light weight, ease of processability, and low cost. Electroactive properties of soft matter have been long known, starting with Galvani's frog's legs in the 1780's. More recently, the discovery of large electrostrictive strain in electron-irradiated poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer by Zhang and collaborators¹ showed the possibility of using electric-field-induced and reversible phase transitions between polar and nonpolar structures of [P(VDF-TrFE)] to achieve large strains ($\sim 7\%$) at high frequencies (up to ~ 10 kHz) leading to very good energy densities, similar to those in piezoceramics.^{2,3}

In this letter, we use atomistic computer simulations to explore the possibility of improving the electromechanical properties of PVDF-based nanoactuators by controlling and optimizing their structure at the molecular level. Nanoscale actuators and motors play a central role in nanotechnology, and atomistic modeling is a powerful tool to design and test nanodevices in a fast and cost-effective manner, postponing issues of fabrication until a promising design is found.

Four crystalline polymorphs of PVDF have been well characterized experimentally^{4,5} and theoretically.⁶ They are generally referred to as I, II, III, and IV, and differ by the conformation of their chains and their relative orientation.⁴⁻⁶ Phase I is formed by all-trans (all-I) bonds with chain dipoles

arranged in a parallel fashion leading to a polar crystal. Phases II and IV are formed by chains with $TGTG'$ (G = gauche) conformations arranged in an antiparallel and parallel manner, respectively. Phase III contains T^3GT^3G' chains making a polar crystal. *Ab initio* calculations predict Phase II to be the most stable one.⁷

Unfortunately, large energy barriers must be overcome to modify the polymer structure, making the transformation between phases difficult. Switching the direction of polarization in PVDF leads to very large polarization hysteresis. Zhang and collaborators¹ showed that high-energy electron irradiation of a random copolymer of PVDF with TrFE results in hysteresis loops and large electrostrictive strains. X-ray diffraction, Fourier transform infrared spectroscopy, and differential scanning calorimetry have been used to characterize the microstructural changes induced by the irradiation.² Reduction of the crystallinity of the sample, decreasing the size of the polar domains below a critical value where the crystalline regions transform to a nonpolar combination of T and G bonds (mainly formed by T_3G segments). This nanostructural change leads to a desirable decrease in polarization hysteresis by lowering the nucleation barriers. The excellent electromechanical properties of the irradiated copolymer result from two key characteristics:

- (1) A reversible phase transition between a ground-state structure composed of T and G bonds and one obtained under an external electric field composed by all- T chains.
- (2) Low-energy barriers involved in the (reversible) phase transition.

The design of our nanoactuator is based on the observation that an isolated PVDF chain in equilibrium contains a combination of T and G bonds, and that this configuration can be transformed to all- T bonds with an external field involving small activation barriers and in short time scales. Thus, it may be possible to achieve the two conditions nec-

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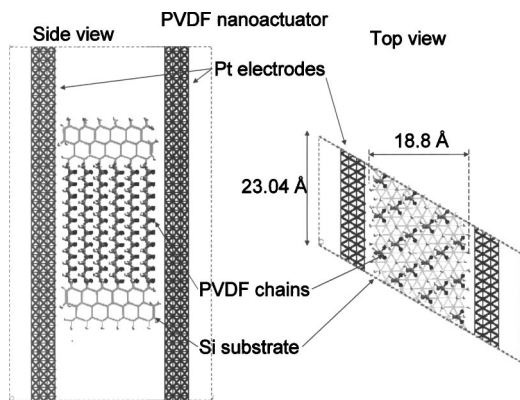


FIG. 1. Nanoactuator: The PVDF chains are assembled between two unreconstructed $\langle 111 \rangle$ Si surfaces with one-half of coverage. Two Pt slabs are placed on opposite sides of the actuator (the distance between the Pt slabs is 23 Å). The zero field distance between Si surfaces is 24.5 Å.

essary for good actuation properties by controlling the chain packing density to obtain an intermediate state between the densely packed crystal (high activation barriers and nonreversible phase transitions) and an isolated chain (low activation barrier but also minimal energy density). The desired control over packing density can be achieved by assembling by the polymer chains in a crystalline substrate, as shown in Fig. 1.

We covalently bond 10-monomer long PVDF chains on a $\langle 111 \rangle$ Si surface using one-half of the available sites (the rest are passivated with hydrogen atoms, in practice these might also have been C1 atoms); a second Si slab is bonded to the opposite end of the chains, see Fig. 1. We position two parallel Pt slabs on opposite sides of the actuator. The slabs are two face-centered-cubic unit cells thick covering the whole area of the simulation cell ($a=50$ Å, $b=23.04$ Å, $c=75$ Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$); they are used to generate a homogeneous electric field inside the actuator. The simulation cell is periodic in the plane of the Pt electrodes in the direction perpendicular to the polymer chains. We describe the PVDF chains using the first-principles-based MSXX force field that has been widely used to describe electromechanical properties of PVDF.^{6,8,7} In this study, we turned off the cross terms of the interactions to make the computations more tractable; the main role of cross terms is fine tuning the vibrational properties but they do not have an important effect on torsional energy barriers (the most important factor governing the nanoactuator performance). The Si atoms are described by a simple force field and are not critical for the results in this letter. The only role of the Pt atoms is to provide the electric field, and their atomic positions are fixed during the dynamical simulations. The atoms forming the lowest monolayer of the bottom Si slab are also fixed.

We thermalized the system with constant temperature molecular dynamics (MD) simulations at $T=300$ K; this leads to chains containing T and G bonds. We then follow the dynamics of the actuator under the influence of an external field: The Pt atoms in the external half of each electrode are assigned a time dependent charge: $q(t) = \pm q_0 \sin(2\pi\omega t)$. This leads to a spatially uniform electric field acting on the actuator, equal to the surface charge density, with a harmonic variation in time and amplitude E_0 . We simulate the dynamical response of the actuator in the presence of the electrical stimulus via constant energy MD with a time step of 1 fs and

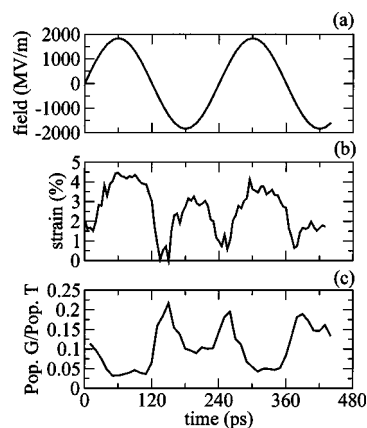


FIG. 2. Time evolution of the external electric field (a), device strain (b), and fraction of G bonds (c) for $\omega=4.166 \times 10^9$ Hz and $E_0=1840$ MV/m.

updating the charges on the electrode atoms every 5 ps (5000 MD steps).

Figure 2 shows the results for $\omega=4.166 \times 10^9$ Hz (corresponding to a period of $T=240$ ps) and $E_0=1840$ MV/m. This electric field results from assigning a charge 0.1e to the atoms in one slab and $-0.1e$ to the ones in the opposite slab; 480 atoms are charged in each slab and the area is 3750 Å². We show the time evolution of the applied field [Fig. 2(a)], the device uniaxial strain [$(\ell(t)-\ell_0)/\ell_0$, where $\ell(t)$ is the separation between the Si slabs and ℓ_0 corresponds to zero applied field; Fig 2(b)] and the ratio between G and T bonds [Fig. 2(c)]. We see from Fig. 2 that the actuator is able to respond to the applied field and change its conformation accordingly. For large applied electric fields, the strain is positive regardless of the direction of the field; this corresponds to all- T configurations with the polymer polarization direction depending on the sign of the applied field. For zero field, the polymer conformation contains T and G bonds and the chains are shorter (zero strain), see Fig. 2. Figure 2 shows that our design can reach very large strains ($\sim 4.5\%$) at extremely high frequencies (over 10^9 Hz). The strains are comparable with those obtained experimentally for irradiated P(VDF-TrFE) at much lower frequencies (and also weaker fields) and are much larger than those in widely used ceramics ($\sim 0.1\%$).

Figure 3 shows the strain-polarization curves obtained from MD simulations corresponding to $E_0=1840$ MV/m and two frequencies: $\omega=4.166 \times 10^9$ Hz ($T=240$ ps) and $\omega=8.333 \times 10^9$ Hz.

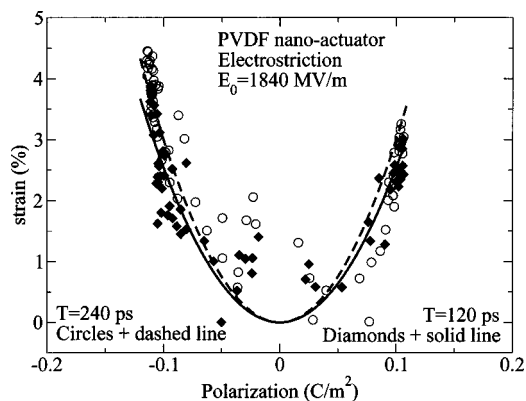


FIG. 3. Strain as a function of polarization obtained from our MD simulation for $E_0=1840$ MV/m and two frequencies: $\omega=4.166 \times 10^9$ Hz and $\omega=8.333 \times 10^9$ Hz.

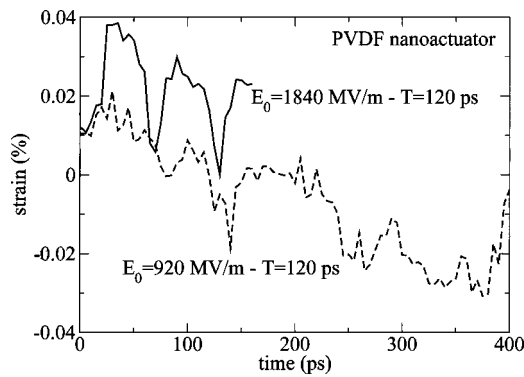


FIG. 4. Strain as a function of time obtained from MD simulations corresponding frequency $\omega=8.333 \times 10^9$ Hz and two electric-field strengths 1840 MV/m (solid line) and 920 MV/m (dashed line).

$=8.333 \times 10^9$ Hz ($T=120$ ps). We can see that our actuator follows the electrostrictive relationship between strain and polarization ($\epsilon=QP^2$) for both cases. We obtain $Q=3.01$ (C/m^2)⁻² for $\omega=4.166 \times 10^9$ Hz and $Q=2.55$ (C/m^2)⁻² for $\omega=8.333 \times 10^9$ Hz. The predicted electrostrictive coefficients of the nanoactuator are slightly larger than those of P(VDF-TrFE) copolymers in the ferroelectric phase [$2.1\text{--}2.5$ (C/m^2)⁻²] (Ref. 9) but smaller than those of electron irradiated samples [13.5 (C/m^2)⁻²],¹ these experiments were conducted at frequencies much lower than those of the simulations.

We see from Figs. 2 and 3 that for $E_0=1840$ MV/m, the nanoactuator is able to follow the electric field for $\omega=4.166 \times 10^9$ and 8.333×10^9 Hz; the maximum strain is slightly lower (about 4%) for the higher-frequency case. If we decrease the electric field by one-half ($E_0=920$ MV/m)

and keep the frequency at 8.333×10^9 Hz, the device does not work; the chains are not able to switch fast enough. This can be seen in Fig. 4 where we show the time evolution of the nanoactuator strain for $\omega=8.333 \times 10^9$ Hz and two electric-field strengths 1840 MV/m and 920 MV/m. This shows that atomistic simulations can predict the range of optimum performance of a given device, making it a very useful tool for materials design.

In summary, we use atomistic simulations to show that very large strains ($\sim 5\%$) at extremely high frequencies (over 10^9 Hz) can be obtained in a PVDF actuator by controlling the packing density of the polymer chains. These desirable properties are obtained by making use of the fast reversible structural transition from chains containing a combination of T and G bonds at zero field to all- T conformation under an external electric field. Our work exemplifies the important role that modeling can play in the design of new materials and devices with improved properties.

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