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Why are Ferroelectric Polymers Difficult to Find – And Difficult to Verify

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The field of electrets encompasses a wide range of materials that maintain an external electric field due to alignment of internal electric dipoles or trapped charge, or both [1]. Polymers incorporating molecular dipoles constitute an important class of electrets, and so it is fitting that we consider the conditions under which such a polymer can also be considered a ferroelectric [2]. Further, because ferroelectric polymers have many uses, it is fruitful to consider how their properties depend on molecular structure [3].

The commonly accepted definition of ferroelectricity is quite simple. There must be a permanent electrical polarization that can be reversed, repeatedly, by an opposing electric field [2]. The existence of a permanent, meaning thermodynamically stable, polarization necessarily limits bulk ferroelectricity to crystalline systems, specifically those with one of the 10 polar crystal point groups, out of 32 distinct point groups. The prototypical ferroelectric is barium titanate, which is a so-called “displacive” ferroelectric characterized by a small (1%) ionic displacement within the unit cell that forms spontaneously as the crystal is cooled from the cubic paraelectric phase to the tetragonal ferroelectric phase. Polarization switching is accomplished by collective ion tunneling between equivalent positions on opposite sides of the cell center. Another class of ferroelectrics is the so-called “order-disorder” materials characterized by a transition from randomly oriented dipoles in the paraelectric phase to ordered dipoles in the ferroelectric phase. The class of order-disorder ferroelectrics includes proton-tunneling systems like KH_2PO_4 and molecular ferroelectrics like sodium nitrite, thiourea, and polyvinylidene fluoride (PVDF, $-\text{CH}_2-\text{CF}_2-$) [3].

The reversibility of the polarization is a further restriction eliminating materials that are merely pyroelectric, materials that do have a permanent polarization, but for some reason, usually steric hindrance, the electric dipoles cannot be reversed in place. This is illustrated in Fig. 1, which shows two ferroelectric polymer crystals. In Fig. 1a, the molecules are compact and are able to rotate in place. In Fig. 1b, the molecules are quite elongated compared to their separation,

and therefore they interfere with each other when rotating. In the extreme case of highly elongated molecules, the only way to reverse the polarization, besides the trivial trick of rotating the crystal by 180° , is to take it apart, reverse the dipoles, and put it back together. This crystal is merely pyroelectric.

Since the discovery of piezoelectricity in polyvinylidene fluoride (PVDF, $-\text{CH}_2-\text{CF}_2-$) [4] and subsequent confirmation of ferroelectricity in copolymers of VDF, e.g., with trifluoroethylene [5,6], evidence for ferroelectricity has been found in only a small number of crystalline polymers. (I exclude here ferroelectric liquid crystals, where polarization is only a secondary order parameter.) PVDF stands out because of its highly compact structure and large fixed dipole moment. Nearly any variation in structure adversely affects chemical stability, crystallinity, or rotational mobility.

Returning to the PVDF prototype (Fig. 1a), perhaps we can make some substitutions to optimize certain characteristics. One promising proposal is to further break the symmetry of the backbone by replacing the carbons with boron and nitrogen to form the polyethylene analog polyaminoborane, $-\text{BH}_2-\text{NH}_2-$, or the PVDF analog, polyaminodifluoroborane $-\text{BF}_2-\text{NH}_2-$. *Ab initio* calculations predict that these should have approximately double the polarization of PVDF [8]. Unfortunately, these compounds are highly reactive and therefore difficult to handle and process. Another variation on the PVDF theme is to replace the fluorines with other electronegative units, like Cl, acetate, or $\text{C}=\text{N}$, as in polyvinylidene cyanide (PVCN, Fig 1b). Such substitutions either make the crystal structure more open, reducing the intermolecular interactions necessary for stabilizing ferroelectric order, or they suffer from steric interference, greatly hindering polarization switching. Although early studies [7] focused on amorphous forms of PVCN, which cannot be ferroelectric, more recent studies find evidence for ferroelectricity in crystalline samples [9].

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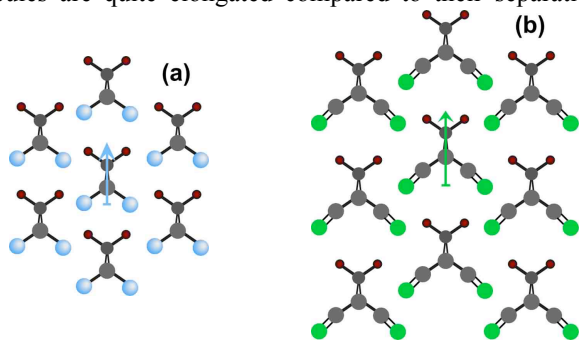


Fig. 1. End view of all-trans β phase crystals of: (a) PVDF; (b) PVCN.