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Ferroelectric Polymers

Andrew J. Lovinger

Because of their widespread use as electrical insulators, synthetic polymers have generally come to be regarded as electrically passive. However, in the past two decades, polymeric materials have been developed that can be used as active elements of an electrical circuit; most of these are piezoelectric, although, very recently, polymers that can be made electrically conductive have also appeared. Piezoelectric polymers have elicited much interest because of their many realized and potential applications as electromechanical transducers, for which they are particularly well suited as a result of their easy processability into thin, light, tough, and flexible films.

Summary. Piezoelectricity and pyroelectricity, traditionally encountered in certain single crystals and ceramics, have now also been documented in a number of polymers. Recently, one such polymer—poly(vinylidene fluoride)—and some of its copolymers have been shown to be ferroelectric as well. The extraordinary molecular and supermolecular structural requirements for ferroelectric behavior in polymers are discussed in detail, with particular emphasis on poly(vinylidene fluoride). Piezoelectric, pyroelectric, and ferroelectric properties are also briefly reviewed, as are some promising applications of such polymers.

By the simplest and broadest definition, a piezoelectric material is one that undergoes a change in electrical polarization in response to mechanical stress (or vice versa). From a solid-state viewpoint, piezoelectricity is defined in a much more rigorous and restricted sense as an intrinsic property of only certain crystal classes. The criteria can be made successively more specific to distinguish two important related properties—pyroelectricity and ferroelectricity. Of the 32 crystal classes into which all crystalline materials may be categorized, some have symmetry elements that render them nonpolar; other, noncentrosymmetric, crystal classes can exhibit polarization, and it is these that are rigorously defined as piezoelectric. Some such piezoelectric crystals develop polarization only when stressed, while others are permanently polar; the latter crystals will respond not only to stress but also to changes in temperature, and are therefore termed pyroelectric. A final subdivision yields the ferroelectric crystals: these also have a unique polar axis, whose direction can be reoriented by application of an electric field. A ferroelectric crystal is thus a pyroelectric one that exhibits reversible polarization.

In view of the complex molecular, crystalline, and morphological structure of polymers, it may appear surprising that any exist which comply with the very restrictive requirements of ferroelectricity. Nevertheless, in the past few years at least one polymer, poly(vinylidene fluoride), and some of its copolymers have been shown to be ferroelectric, while other piezoelectric polymers are also likely candidates. Poly(vinylidene fluoride) (abbreviated PVF_2), whose molecular repeat formula is $(CH_2\text{–}CF_2)_n$, exhibits by far the strongest piezoelectric and pyroelectric activity of all known polymers. These two properties were first reported in 1969 and 1971 (*1*), respectively, and many actual and potential applications of PVF_2 have been described since then.

The primary goal of this article is to explain the extraordinary characteristics of structure, at all its levels, that must be combined to render a polymer ferroelectric. These are illustrated by investigating in detail the monomeric, macromolecular, crystalline, and morphological structure of PVF_2 and distinguishing it at all these levels from that of other polymers; copolymers of PVF_2 and other piezoelectric (and potentially ferroelectric) polymers are covered more briefly. Macroscopic polarization of samples and their consequent electrical behavior are also discussed; the article then concludes with a brief description of applications of PVF_2. The treatment is necessarily condensed, but extensive reviews are available (*2*–*6*). No attempt is made to discuss related materials, such as those in the important categories of (i) piezoelectric and pyroelectric biopolymers, and (ii) polymeric transducers ("electrets") whose piezoelectric behavior is not of inherent dipolar origin but results from injection of charges; comprehensive reviews exist for both categories [(*7*) and (*8*), respectively].

Structure

Monomeric. Macromolecular chains consist of many elementary repeating units, called monomers, that have been chemically linked during polymerization. Many monomers contain polar chemical groups. To yield useful piezoelectric polymers, their constituents should not be so bulky as to prevent crystallization of the macromolecules or to force them into shapes (such as helical) that cause extensive internal compensation of polarization; the resulting macromolecules should also be chemically stable and not cross-linked into infusible and insoluble solids. In light of these considerations, fluorocarbons are highly appropriate monomers to yield piezoelectric polymer

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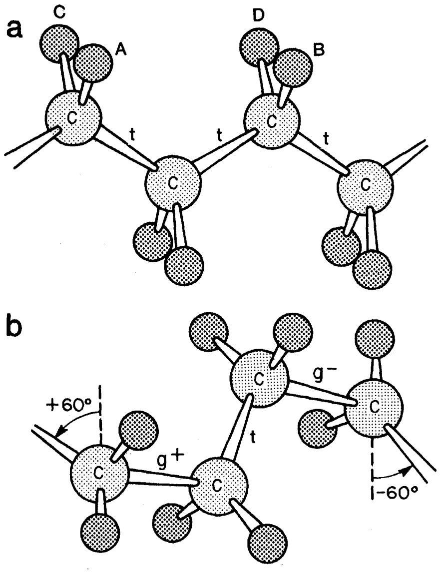


Fig. 1. Schematic representation of polymer chain segments in different conformations: (a) *ttt* and (b) g^+tg^-.

crystals. The fluorine atom is very small, its van der Waals radius (1.35 angstroms) being only slightly larger than that of hydrogen (1.2 Å), and it forms highly polar bonds with carbon, having a dipole moment $\mu = 6.4 \times 10^{-30}$ coulomb-meter [the traditional unit of μ—the debye—is expressed in the metric system as 3.34×10^{-30} C-m]. Common resulting polyfluorocarbons are PVF_2, plus poly(vinyl fluoride) [PVF, molecular formula $(CH_2–CHF)_n$] and polytrifluoroethylene [PF_3E, $(CF_2–CHF)_n$]. Other polar groups that can be expected to lead to useful piezoelectric polymers include C–Cl ($\mu = 7.0 \times 10^{-30}$ C-m) and C–CN ($\mu = 12.9 \times 10^{-30}$ C-m); typical polymers incorporating these groups are poly(vinyl chloride) [PVC, $(CH_2–CHCl)_n$], poly(vinylidene chloride) [PVC_2, $(CH_2–CCl_2)_n$], and polyacrylonitrile [PAN, $(CH_2–CHCN)_n$]. A further possibility is associated with the highly polar hydrogen bond, C=O---H–N ($\mu = 12.0 \times 10^{-30}$ C-m) found in polyamides. We will see how successively higher levels of structure affect all these possibilities and how PVF_2 has emerged as the strongest piezoelectric and pyroelectric polymer with clearly demonstrated ferroelectric behavior.

Chain configuration. This term pertains to the stereochemical manner in which monomers are linked together; it thus describes characteristics of a macromolecule that can be altered only by cleavage of chemical bonds and that are, in effect, immutable after polymerization. The monomers listed above have a directionality (*9*); if we use PVF_2 as an example and denote $-CH_2$ as the "head" of the monomeric unit and $-CF_2$ as its "tail," we usually have regular head-to-tail sequences but can also have reversed monomeric addition leading to head-to-head and tail-to-tail defects. Evidence from nuclear magnetic resonance spectroscopy shows that most monomers are added "isoregically" (that is, head to tail in the same direction) during polymerization of PVF_2 (95 to 97 percent), but less regularly so in the case of some other polymers—for example, 88 to 90 percent in PVF and 87 to 89 percent in PF_3E (*10*). Moreover, head-to-head defects are generally followed by tail-to-tail addition (*10*), which causes the average dipole moment of the chain per monomeric unit to be reduced by only 6 to 10 percent in PVF_2 but 20 to 24 percent in PVF and 22 to 26 percent in PF_3E.

A second type of configurational defect commonly seen in vinyl polymers and trifluoroethylene results from their stereochemically asymmetric carbon atoms. Using PVC as an example, we can see with the aid of Fig. 1a that the chlorine atoms could be either always on the same side of an extended carbon chain (positions A and B or C and D), or regularly alternating (A and D or B and C), or randomly located. Although special techniques and catalysts exist that promote stereoregular addition, vinyl polymers are most commonly available only in "atactic," or random, configurations that render them (with few exceptions, such as PVF) incapable of entering into crystallographic lattices and thus excluded from possible ferroelectric behavior. On the other hand, vinylidene polymers, not having asymmetric carbon atoms, are immune from such considerations of tacticity.

Chain conformation. In the melt or in solution, polymer chains have randomly coiled shapes (conformations), which configurationally disordered macromolecules are, to a great extent, forced to retain in their solid state as well; however, chains free from configurational defects can crystallize into regular conformations when cooled from the melt. This is accomplished by rotation about single bonds in a manner that minimizes the potential energy of the chains arising from internal steric and electrostatic interactions. The most favorable torsional bond arrangements have substituents at 180° to each other (called *trans* or *t*) or at ± 60° (*gauche*$^\pm$ or $g^\pm$); actual torsional angles commonly deviate somewhat from these values. A sequence of three *t* bonds is illustrated in Fig. 1a and a g^+tg^- in Fig. 1b.

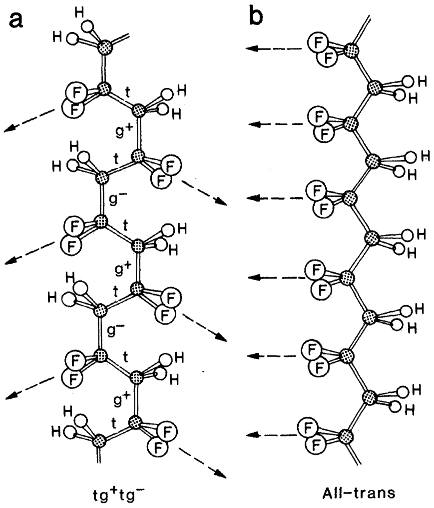


Fig. 2. Schematic depiction of the two most common crystalline chain conformations in PVF_2: (a) tg^+tg^- and (b) all-*trans*. The arrows indicate projections of the $-CF_2$ dipole directions on planes defined by the carbon backbone. The tg^+tg^- conformation has components of the dipole moment both parallel and perpendicular to the chain axis, while the all-*trans* conformation has all dipoles essentially normal to the molecular axis.

The molecular chains of most polymers are restricted by steric and electrostatic intramolecular interactions into one regular conformation of lowest potential energy. In this regard PVF_2 stands out from its counterparts, in that it can adopt at least three regular conformations (of similar potential energies) for reasons associated with the van der Waals radii of its constituents. PVF_2 is in the middle of a family of polyfluoroethylenes, whose general repeat formula is $(CH_aF_{2-a}–CH_bF_{2-b})_n$ with *a* and *b* = 0, 1, or 2. Macromolecules of that class that are rich in hydrogen (the smallest possible chain substituent)—that is, polyethylene, $(CH_2–CH_2)_n$, and PVF, $(CH_2–CHF)_n$—will encounter only low rotational barriers separating their possible conformations; as a result, they will easily reach the lowest-energy conformation (the all-*trans*) and adopt only that. At the other end of the spectrum are members rich in the somewhat bulkier fluorine—that is, PF_3E, $(CF_2–CHF)_n$, and polytetrafluoroethylene, $(CF_2–CF_2)$; in these, rotation is now sterically quite hindered, so that they are forced to adopt the one conformation of least discomfort (such a conformation is invariably helical or quasi-helical). PVF_2 molecules, containing two hydrogen and two fluorine atoms per repeat, are intermediate between these two extremes: they have a choice of multiple conformations, as do their hydrogen-rich counterparts, yet because rotational barriers are now high, the chains can also be stabilized into favorable conformations other than that of lowest energy.

The three known conformations of PVF_2 (*11–13*) are all-*trans*, tg^+tg^-, and $tttg^+tttg^-$ (in all cases there are slight deviations from the 180° and ±60° torsional angles). The first two conformations are by far the most common and important ones and are depicted schematically in Fig. 2. Because of the alignment of all its dipoles in the same direction normal to the chain axis, the all-*trans* is the most highly polar conformation in PVF_2 (7.0×10^{-30} C-m per repeat). The tg^+tg^- conformation is also polar, but because of the inclination of dipoles to the molecular axis (Fig. 2), it has components of the net moment both perpendicular (4.0×10^{-30} C-m) and parallel (3.4×10^{-30} C-m) to the chain; approximately the same values also characterize the $tttg^+tttg^-$ conformation.

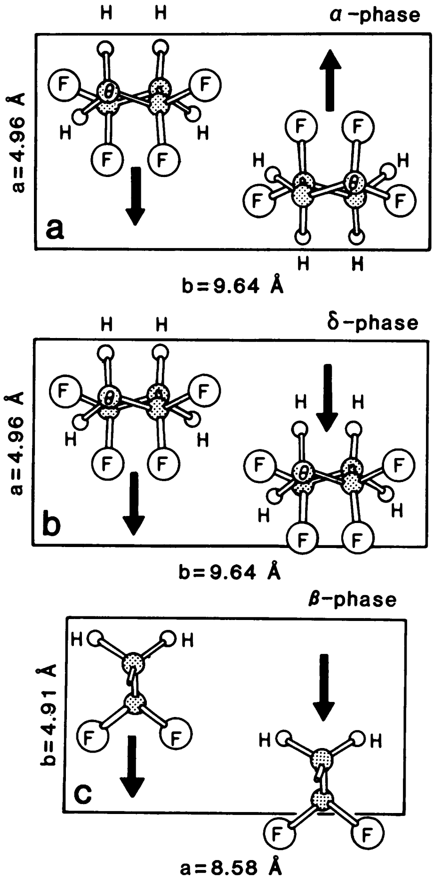
It is interesting to note that, for the reason discussed above, PVF differs from other stereoirregular macromolecules in that its atacticity does not prevent it from crystallizing with a regular conformation (all-*trans*); while its dipole moment per repeat is about 50 percent that of PVF_2, regicity defects reduce its overall value for the chain still further.

Chain packing. The ability of molecules of PVF_2 and of other polymers to adopt polar conformations is not sufficient to ensure polarity of their resulting crystals, for these molecules may be crystallographically packed in a lattice so as to cancel each other's moment. For instance, the most common polymorph of PVF_2, the α-phase, which may be obtained by melt-solidification at all temperatures, suffers from exactly such cancellation. As may be seen in Fig. 3a, the unit cell of the lattice of α-PVF_2 consists of two chains in the tg^+tg^- conformation, whose dipole components normal to the chain axes are antiparallel, thus neutralizing each other (*11*). The disposition of axial components of the dipole moment has been controversial, with suggestions of a regular antiparallel packing (*11*) (that is, one chain as in Fig. 2a, adjacent to one whose C–F dipoles point up) or of a statistical arrangement (*12*); however, recent evidence (*14*) lends support to both by showing that α-chains are generally under statistical packing, which becomes regularly antiparallel upon heat treatment at high temperatures.

Although the dipole moments of tg^+tg^- chains in the α-unit cell are internally compensated, a polar analog (called the δ-phase) can be obtained by application of a high electric field to films of this polymorph (*15*); in effect, this involves rotation of every second chain by 180° about its axis, so that molecules are now packed with the transverse components of their dipole moments pointing in the same direction (Fig. 3b). It is unlikely that chains rotate as physically rigid units; dipole reversal may rather involve propagation of a twist wave along the chains (*16*) or small intramolecular rearrangements (*17*).

The most highly polar phase of PVF_2 is the β-phase, whose unit cell consists of two all-*trans* chains packed with their dipoles pointing in the same direction (*11*) (Fig. 3c); an antipolar analog of this phase is not known. Packing of chains in β-PVF_2 is such that fluorine and hydrogen atoms of neighboring chains are approximately at the same level parallel to the *a*-axis of the unit cell (Fig. 3c); this very favorable intermolecular contribution to the potential energy plays a major role in stabilizing the crystalline structure of β-PVF_2. Chains of the $tttg^+tttg^-$ conformation are packed in a polar fashion to yield the γ-phase of PVF_2 (*13*). Its unit cell has the same base dimensions as that of its α-counterpart (Fig. 3a), a fact that enables a solid-state transformation from α-PVF_2 to the thermodynamically more stable γ-phase to occur at high temperatures (~ 160°C) solely through limited intramolecular motions (*18*). A nonpolar analog of γ-PVF_2 has also been reported but may exist only within a mixture of phases obtained at very high temperatures (*14*). This wealth of crystalline phases for PVF_2 is very unusual among polymers (where one or two polymorphs are common) and is another reflection of its unique molecular structure. PVF, on the other hand, crystallizes with only one unit cell that is essentially identical to that of β-PVF_2.

Morphology. We have seen so far that polarization of individual chemical groups can survive in a noncompensatory manner through successively higher levels of structure to yield individually polar crystals. However, polymer crystals are extremely small and, when grown from the melt, are arranged into essentially spherically symmetric polycrystalline aggregates that have no net polarization. These aggregates are called spherulites and result from nucleation of primary crystals within the melt, fol-



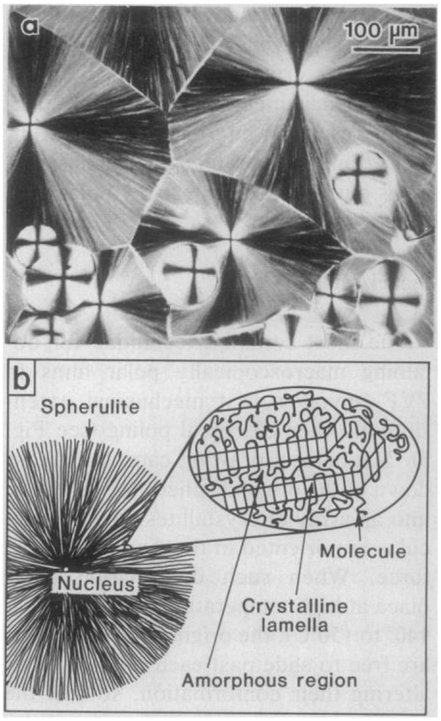


Fig. 3 (left). Unit cells of (a) the α-phase, (b) the δ-phase, and (c) the β-phase of PVF_2 shown in projection parallel to the chain axes. Arrows indicate dipole directions normal to the molecular axes. Fig. 4 (right). (a) Typical appearance in the polarizing microscope of spherulites of PVF_2 crystallized from the melt at 160°C. The large spherulites are of the antipolar α-phase; the small ones belong to the polar γ-phase. The dark crosses correspond to the optical polarization directions of the microscope. (b) Schematic representation of the structure of polymer spherulites.

lowed by radial growth outward from these nuclei in spherical envelopes (*19*). PVF_2 melts at ~ 170° to 200°C (depending on polymorphic form and crystallization temperature) and when cooled from the melt crystallizes in the form of spherulites of the nonpolar α-phase; at high temperatures of crystallization, γ-spherulites are also obtained (*18*). The β-phase is not usually produced from the melt since that requires high pressures (*20*) or epitaxial techniques (*6*), but is obtained by mechanical deformation or electrical poling as described in the next section. Typical spherulites of α- and γ-PVF_2 are seen in Fig. 4a, and a schematic representation of their microstructure is depicted in Fig. 4b. This microstructure is such that what appear in the optical microscope as radial fibers are, in fact, stacks of very thin, platelet-like crystals called lamellae (about 10 nanometers thick and several micrometers in lateral dimensions). These lamellae consist of macromolecular segments that are packed crystallographically, while the intervening amorphous regions contain chain segments in disordered conformations; this two-phase structure of the solid state is typical of crystallizable polymers. In PVF_2, crystalline lamellae represent about 50 percent of the total mass, the other half being amorphous. In summary, our review of structure has shown that, while some polymers can form polar crystals, their three-dimensional arrangement in macroscopic specimens results in internal electrical compensation. To overcome this, such specimens must then be externally polarized.

Polarization

The most common technique for obtaining macroscopically polar films in PVF_2 involves first mechanical extension and then electrical poling (see Fig. 5). Mechanical drawing causes a breakdown of the original spherulitic structure into an array of crystallites whose molecules are oriented in the direction of the force. When such deformation takes place at high temperatures (for instance, 140° to 150°C), the original tg^+tg^- chains are free to slide past each other without altering their conformation, so that the resulting structure is still of the nonpolar α-phase. However, when the deformation is conducted below ~ 90°C, where the polymer is much stiffer, the molecular chains are also forced into their most extended possible conformation, which is the all-*trans*: its monomeric repeat corresponds to 2.56 Å compared to 2.31 Å for the tg^+tg^- (see also Fig. 2). Therefore, mechanical extension at low temperatures has the advantages of producing not only a molecularly oriented morphology, but also one belonging to the polar β-phase. However, as may be seen with the aid of Fig. 5, the dipole vectors are still not uniquely oriented but lie randomly in planes normal to the molecular chains. The final step that is therefore required to produce a macroscopically polar specimen is to align these dipoles in the direction of an externally applied field normal to the film. This is usually accomplished by evaporating electrodes on the sample and connecting them to a high-voltage source supplying a field of at least 0.5 megavolt per centimeter (*21*), or by using plasma or corona poling (*22*). The facility of field-induced dipole reorientation in β-PVF_2 is related to the pseudohexagonal packing of its chains (*23*) (a check of the unit cell base dimensions in Fig. 3c will confirm that they differ only by about 1 percent from hexagonal); this is obviously a factor of major importance in facilitating ferroelectric switching in β-PVF_2, and suggests that this phenomenon takes place in 60° increments (*23*). Films of the α-phase can also be poled: at intermediate fields (1 to 3 MV/cm), the tg^+tg^- chains preserve their conformation, but are packed in a polar unit cell (α → δ transformation), whereas at higher fields (~ 5 MV/cm) they are further transformed both intra- and intermolecularly to the β-phase.

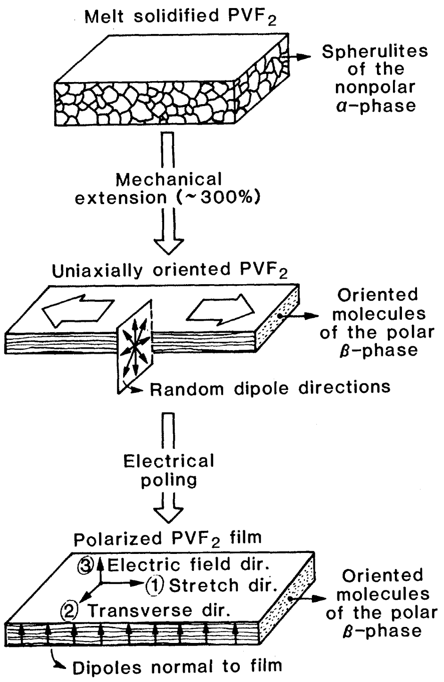


Fig. 5. Schematic representation of the processes commonly employed to obtain piezoelectrically and pyroelectrically active films of PVF_2.

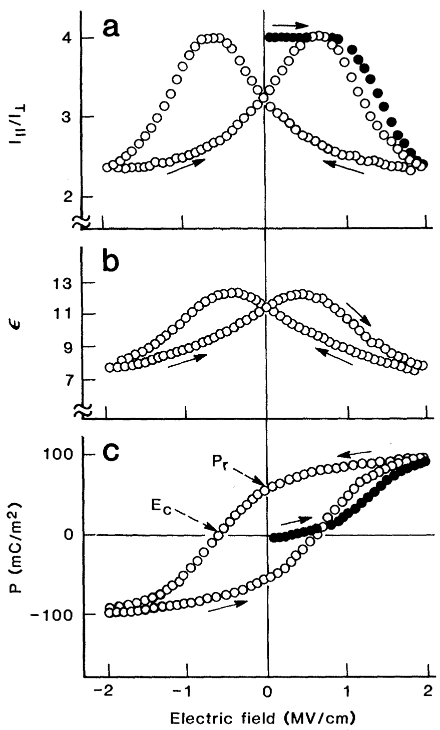
Ferroelectricity in PVF_2

Whether PVF_2 is a true ferroelectric rather than a trapped-charge electret was a controversial issue for about a decade after the discovery of its strong piezoelectricity; despite its clearly dipolar crystalline structure, there was evidence that polarization is inhomogeneous across the thickness of PVF_2 films (being much higher at the side facing the positive electrode), so that piezoelectricity might simply have been a result of trapped charges injected by the electrodes (*24*). It has now been shown that this anisotropy disappears at high poling fields, that dipoles are, in fact, reoriented during application of an electric field, and that other typical phenomena accompanying ferroelectricity—hysteresis loops and Curie transitions—are also seen in PVF_2.

Dipolar reorientation has been proved by x-ray (*4*) and infrared (*25*) techniques; results from the latter are depicted in Fig. 6a. Here, the ratio of infrared intensity from a β-PVF_2 sample parallel to the molecular chains ($I_{\|}$) and perpendicular to them ($I_{\perp}$), the latter parallel to the $-CF_2$ dipole moment, is seen to vary with electric field and to be reversible in a hysteresis-like fashion typical of a ferroelectric. Simultaneously obtained curves of dielectric constant, ε, versus poling field show similar behavior (Fig. 6b). What has broadly been considered the most characteristic experimental manifestation of ferroelectricity is the hysteresis behavior of polarization as a function of electric field. Such a curve is also observed for β-PVF_2 in Fig. 6c, which shows that polarization rises with applied field, that a "remanent polarization" (P_r in Fig. 6c) persists after the field has been returned to zero, that a negative "coercive field" (E_c in Fig. 6c) is required to depolarize the sample, and that polarization can be repeatedly reversed by cycling the field between ±2 MV/cm.

At this stage we may inquire as to what renders PVF_2 a ferroelectric instead of simply a pyroelectric material whose dipole directions are stable rather than reversible. For the β-phase, the pseudohexagonal character of its lattice clearly plays a major role (*23*). However, the exceptional molecular structure of PVF_2 detailed above is also a critical factor, for chains of highly anisotropic cross section, with bulky protrusions or pendant groups, would most likely be locked in place and not allow facile inter- or intramolecular dipole reorientation. The importance of chain structure in this regard is seen in the ferroelectric switching of the δ-phase, whose unit cell is far from hexagonal (Fig. 3, a and b), and where dipole reversal occurs almost certainly through an intramolecular mechanism (*16*, *17*).

Ferroelectric behavior similar to that of β-PVF$_2$ has also been demonstrated in copolymers of vinylidene fluoride with trifluoroethylene or tetrafluoroethylene; these are randomly added copolymers containing commonly 60 to 80 mole percent VF$_2$. Since they contain a greater proportion of the comparatively bulky fluorine atoms than PVF$_2$, their molecular chains cannot accommodate the tg^+tg^- conformation and are therefore forced to crystallize directly with the more extended all-*trans* conformation (*26*). Copolymers of vinylidene fluoride and trifluoroethylene also exhibit another important aspect of ferroelectricity that so far has not been convincingly demonstrated in PVF$_2$. This is the Curie temperature at which a ferroelectric crystal undergoes reversibly a solid-state transformation to a nonpolar (paraelectric) state. In these copolymers, the Curie transition was found (*27*) to involve primarily intramolecular changes of dipole directions through introduction of $g^{\pm}$ bonds that alter the polar all-*trans* conformation to a somewhat disordered arrangement of $tg^{\pm}$ and tt sequences. Moreover, by extrapolating the observed Curie temperatures as functions of VF$_2$ content to 100 percent VF$_2$, the expected ferroelectric-to-paraelectric transition in β-PVF$_2$ would be in the vicinity of 205°C (*27*)—about 20°C above its melting point—a fact that explains its experimental elusiveness; however, as the conformational changes characterizing these transitions in VF$_2$ copolymers were found (*27*) to span a wide temperature range (30°C or more), the earliest manifestations of such a transition in β-PVF$_2$ should occur in the vicinity of its own melting point.



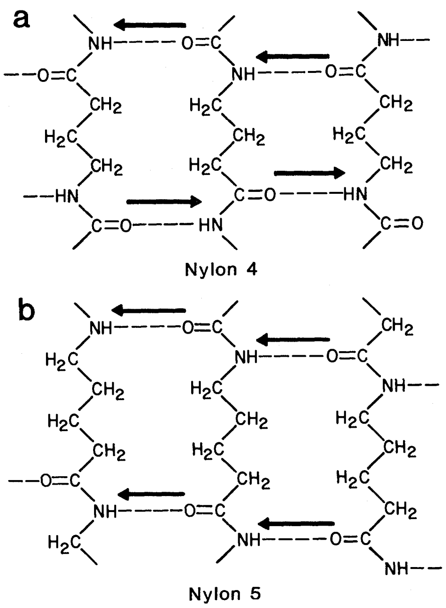


Fig. 6 (left). Variation with applied electric field of (a) infrared absorption at 1273 cm^{-1} corresponding to the $-CF_2$ dipole moment of β-PVF$_2$, (b) dielectric constant, and (c) polarization of a film of β-PVF$_2$. All curves show the hysteresis behavior typical of ferroelectric materials. (●) Initial poling results, (○) results from subsequent poling cycles. [Data from Takahashi *et al.* (*25*) with permission from E. Fukada] Fig. 7 (right). Schematic depiction of hydrogen-bonded sheets in the crystal lattices of (a) even and (b) odd polyamides, showing the dipole directions associated with the hydrogen bonds in each case.

Other Piezoelectric Polymers

Our discussion of structure has shown that most potentially ferroelectric polymers have been eliminated primarily for reasons associated with their chain conformation and packing. Poly(vinylidene chloride), while potentially similar in electrical activity to PVF$_2$, suffers from the presence of bulky chlorine atoms (van der Waals radii, 1.80 Å) which prevent its chains from adopting the highly polar all-*trans* conformation, forcing them instead into one approximating tg^+tg^- or 2$_1$-helical. Another polyfluorocarbon, PVF, although atactic, adopts a structure similar to that of β-PVF$_2$ and is expected to be ferroelectric (although data are lacking). Other polar atactic polymers (such as PVC) are amorphous, yet some piezoelectric response is obtained if an electric field is applied above their glass-transition temperatures (at which molecular motions and rotation of dipoles become possible) and held while the sample is cooled to room temperature to freeze the now oriented dipoles in place. Among the cyanide-containing polymers, polyacrylonitrile suffers from intra- and intermolecular association at its $-C\equiv N$ groups and poly(vinylidene cyanide) is chemically unstable, although a copolymer of the latter with vinyl acetate has been found to exhibit considerable piezoelectric activity (*28*).

However, there exists another class of polymers from the above, whose recently discovered piezoelectric activity is second only to that of PVF$_2$ and which may, in fact, be ferroelectric in nature. This is the class of polyamides (or nylons) of molecular repeat $-HN(CH_2)_{2n}CO-$. Polyamides crystallize in all-*trans* conformations and are packed so as to maximize the number of hydrogen bonds possible between adjacent amine and carbonyl groups, as seen schematically in Fig. 7 for two polyamides containing an even and an odd number of carbon atoms per repeat. The dipoles are clearly associated with the resulting hydrogen bonds, but, as seen in Fig. 7, cancel their net moments in the case of even nylons; it is therefore only the odd members—of which nylon 11, $[HN(CH_2)_{10}CO]_n$, is the most common—that possess a net polarization in their hydrogen-bonded sheets. These sheets are arranged in a polar manner with triclinic symmetry in the common α-phase of such polyamides (*29*); however, at high temperatures (> 90°C) or in rapidly quenched samples the symmetry becomes pseudohexagonal through what is believed to be a randomization of hydrogen bonding, yielding the γ-phase. It has been found (*30*) that films of γ-nylon 11 display high piezo- and pyroelectric activity when poled, while the response of the α-phase is significantly lower. These phenomena are interpreted by breaking of the existing hydrogen bonds and their re-formation in (at least partial) alignment with the field, a process which is indeed more favorable in the pseudohexagonal γ-phase and may explain its higher electrical response (*30*). It should be noted that there exists another category of polyamides having molecular repeats of the type $-HN(CH_2)_xNHOC(CH_2)_yCO-$ which also crystallize in much the same manner; of these, only the "odd-odd" members (those with x and y odd) have their dipoles arranged in a polar unit cell and should thus be expected to behave similarly to nylon 11.

Piezoelectric and Pyroelectric Properties

Although the main purpose of this article is to explain the structural characteristics needed to render a polymer ferroelectric, the piezoelectric and pyroelectric properties of synthetic crystalline polymers are also briefly presented and compared with those of the common ceramics and single crystals.

The piezoelectric and pyroelectric effects are commonly described in terms of compliances between electrical polarization (P) and stress (σ) or temperature (T), respectively, yielding the piezoelectric constant, d, and the pyroelectric constant, p

$$d = \left(\frac{\partial P}{\partial \sigma}\right)_{E,T} \quad \text{and} \quad p = \left(\frac{\partial P}{\partial T}\right)_{E,\sigma}$$

where E is the electric field. The d constant is a tensor whose major components for polymers such as PVF_2 are d_{31}, d_{32}, and d_{33}, the first subscript defining the electric field direction and the second that of mechanical stress; as seen in Fig. 5, in an oriented sample direction 1 is the stretch direction, 2 the transverse, and 3 the film normal.

Realizable values of d and p in PVF_2 depend on a number of parameters, most important of which is the poling field strength; poling temperature plays a small role, while the effects of poling time are significant only up to fields of about 2 MV/cm (*21*). Typical values of the piezoelectric and pyroelectric coefficients, as well as of other physical properties, of materials that have been used as transducers are given in Table 1. The three-dimensional anisotropy of the piezoelectric effect is seen clearly for oriented PVF_2. The d constant associated with the molecular direction (d_{31}) is an order of magnitude greater than that transverse to the polymer chains (d_{32}); both are positive because a stress in the film plane reduces the specimen thickness, thus increasing the surface charge, whereas d_{33} is negative because a stress normal to the film increases its thickness.

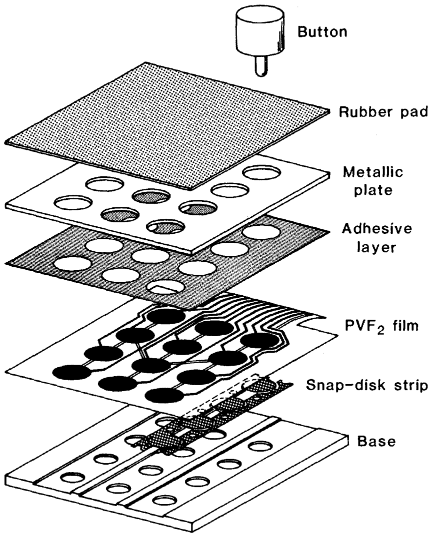


Fig. 8. Schematic drawing of an electrical keyboard with a metallized and polarized PVF_2 film. [From (*37*) with permission from T. R. Meeker]

In comparing the piezoelectric and pyroelectric strengths of the various materials in Table 1, we see that although PVF_2 and its copolymers stand out among other polymeric materials, their activity is an order of magnitude lower than that of the traditional piezoelectric ceramics. However, if we calculate the electromechanical coupling coefficient k_{31} (a quantity reflecting the transducing capability of a material) from $k_{31} = d_{31}\sqrt{c/\epsilon}$ (where c is the stiffness and ϵ the permittivity), we see in Table 1 that, as a result of their very low dielectric constant, PVF_2 and its copolymers appear comparably efficient to ceramics. Moreover, PVF_2 films can sustain about 100 times higher fields than ceramics, so that their power output per unit volume and their maximum elongation per unit field strength (quantities that are proportional to d^2cE^2) are about four to five times greater than in ceramics. Nevertheless, PVF_2 and other polymers are inferior to ceramics in regard to highest temperature of use: piezoelectric constants in PVF_2 reach a maximum at ~ 80°C, where activity begins to fall as a result of increased molecular motions and consequent depolarization; this can be retarded to ~ 110°C by cross-linking the molecules with about 40 megarads of γ-radiation (*31*). However, at even higher temperatures, chemical degradation sets in with loss of HF that increases from α- to γ- to β-PVF_2 as a result of greater steric and electrostatic intramolecular repulsions within *trans*-segments (*6, 32*).

Theoretical models have been developed to describe the macroscopic polarization in films of PVF_2 and to predict values of d and p. The two most applicable models treat PVF_2 as a two-phase system (based on its crystallinity of approximately 50 percent) containing either spherical, charged particles (*33*) or platelet-like polar crystals (*34*) dispersed within an amorphous, nonpolar matrix. Macroscopic piezoelectricity was found to be due not only to the contributions of polar crystallites, but also to a major contribution from the mechanical and electrical heterogeneity between crystalline and amorphous phases (*33*).

Table 1. Typical physical, piezoelectric, and pyroelectric properties of various materials.

Material	Piezoelectric coefficient, d (pC/N)	Pyroelectric coefficient, p (μC/K-m^2)	Density, ρ (g/cm^3)	Elastic modulus, c (GN/m^2)	Dielectric constant, ϵ/ϵ_0	Electromechanical coupling coefficient, k (%)	Acoustic impedance (Gg/m^2-s)
PVF_2 (β-phase)	d_{31} = 20–30 d_{32} = 2–3 d_{33} = −30	30–40	1.8	1–3	10–15	11	2–3
PVF_2 (δ-phase)	d_{31} = 10–17 d_{32} = 2–3 d_{33} = 10–15	10–15					
Other polymers							
VF_2-trifluoroethylene copolymers	d_{31} = 15–30	30–40	~ 1.9		15–20	~ 20	
Poly(vinyl fluoride)	d_{31} = 1	10	1.4	~ 1			
Poly(vinyl chloride)	d_{31} = 1	1–3	1.5	~ 4	3		
Nylon 11 (γ-phase)	d_{31} = 3	3	1.1	1.5	4		
Ceramics and single crystals							
Lead zirconate titanate	d_{31} = 100–300	50–300	7.5	80	1200	30	25
Barium titanate	d_{31} = 80	200	5.7	110	1700	21	25
Quartz	d_{11} = 2		2.7	80	5	10	14

Applications

Piezoelectric and pyroelectric applications of polymers are for the moment confined to PVF_2 (*6*) and take advantage of its extraordinary combination of electrical, mechanical, and acoustical properties. Primary among them are its thinness, light weight, flexibility, toughness, and ability to be formed into intricate shapes. In addition to these and to its good electromechanical coupling discussed above, Table 1 shows that PVF_2 has a much lower acoustical impedance than ceramics (this quantity is proportional to the product of density and stiffness) and is therefore very suitable for acoustical applications in such media as air or water. Such applications have been reviewed (*5, 6*) and include microphones, loudspeakers, headphones, and omnidirectional tweeters, all having essentially flat responses over a broad range of frequencies (*35*). Useful similar applications have also been described in ultrasonics (*36*), particularly as hydrophones (that is, underwater transducers) for which PVF_2 is most appropriate because it consists of light atoms and has therefore a tenfold better acoustical coupling with water than do ceramics. Electromechanical applications include pressure switches, detectors in printing equipment, coin sensors, variable-focus mirrors, impact detectors, medical probes, as well as push buttons and keyboards. The structure of one such keyboard (*37*) is seen in Fig. 8: it consists of a metallized polar PVF_2 film in a holder; films as thin as 16 μm were able to withstand 15 million pushes without failure or deterioration (*37*). Finally, the pyroelectric properties of PVF_2 may be utilized in such devices as infrared detectors, vidicon cameras, security and alarm systems, and electrostatic copiers (*38*).

All of the above demonstrate the usefulness and versatility of PVF_2 and show how the study of structure in polymers can aid in understanding and exploiting the properties of this new class of ferroelectric materials.

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