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ABSTRACT

Ferroelectric polymers entail a number of constraints, which together limit the useful compositional variations. These constraints include the following: a stable molecular dipole moment, compact crystal structure, conformational flexibility, and minimal steric hindrance. They are well satisfied by the prototype ferroelectric polymer, polyvinylidene fluoride, and yet almost every other conceivable molecular structure is limited by comparison.

Index Terms — **ferroelectricity, ferroelectric polymers, vinylidene fluoride, trifluoroethylene.**

1 INTRODUCTION

THE field of electrets encompasses a wide range of materials exhibiting a persistent external electric polarization due to the net alignment of electric dipoles, trapped space charge, or both [1]. Polymers incorporating permanent 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 ferroelectric. Further, because ferroelectric polymers have many uses, it is fruitful to consider how their properties depend on molecular structure.

Polymers readily exhibit three distinct mechanisms of apparent electric polarization [2, 3], namely ferroelectricity, metastable electret orientation, and nonuniform space-charge. These mechanisms are illustrated in **Figure 1**a-c. In the case of ferroelectricity (**Figure 1**a), the material polarization arises from cooperative interactions that favor parallel alignment permanent electric dipoles and is an equilibrium property of the system [4]. Ferroelectrics are defined by bistability of the polarization, as exhibited by polarization hysteresis as the electric field is cycled with an amplitude larger than a characteristic coercive field [4]. The polarization in dipolar electrets (**Figure 1**b), in contrast, is metastable and does not represent an equilibrium ground state [1, 5-7]. The alignment of the dipoles in an electret is primarily a consequence of the external electric field, accompanied by little or no cooperative interaction among the dipoles. Because of the lack of cooperative interaction, the induced polarization is metastable and in the absence of an external electric field, it will relax to a non-polar equilibrium state. The relaxation time can, however, be very long, from seconds to years, resulting in an apparent polarization hysteresis as the dipolar alignment lags behind the applied electric field. The trapped charge in space-charge electrets (**Figure 1**c) will also produce an apparent polariza-

tion [6], in that the electric displacement remains nonzero after the external field is removed. A space charge distribution can also be very long lived if the traps are sufficiently deep [6, 8, 9]. Space-charge electrets exhibit apparent polarization hysteresis due to time lag between field and charge transport or to the nonlinear injection from the electrodes, or both.
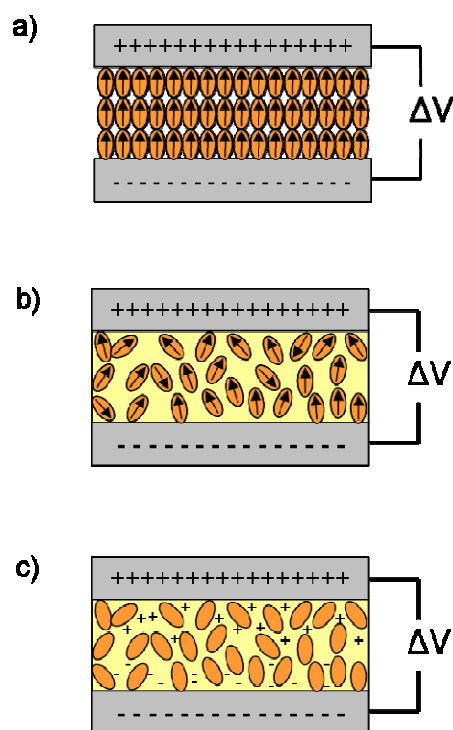
Figure 1. Manifestation of polarization in a) an ordered ferroelectric crystal, b) a dipolar electret, and c) a space-charge electret.

It is not unusual to observe all three of these mechanisms in semi-crystalline dipolar polymers, where polar crystallites, amorphous polymer, and charge trapping may simultaneously exist [6, 10, 11]. As a result, when attempting to characterize

the ferroelectric properties of a given polymer system, care must be taken to insure that the polarization is truly bistable and that polarization reversal is indeed associated with the equilibrium properties of the medium and not external effects, such as injected charge or metastable dipole alignment.

1.1 WHAT IS A FERROELECTRIC?

The commonly accepted definition of ferroelectricity is quite simple. There must be a bistable electrical polarization that can be reversed, repeatedly, by an opposing electric field to produce a polarization hysteresis analogous to magnetization hysteresis in ferromagnets [4, 12]. The existence of a permanent, meaning thermodynamically stable, polarization necessarily limits ferroelectricity to crystalline systems, specifically those with one of the 10 polar crystal point groups [13]. The prototypical ferroelectric is barium titanate, a so-called "displacive" ferroelectric characterized by a small (~1%) net 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 shifting the ions to positions on opposite sides of the cell center [4]. 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 bond-ordering systems like KH_2PO_4 and dipolar-ordering molecular systems like sodium nitrite [14], thiourea [15, 16], and polyvinylidene fluoride (PVDF) [17, 18].

1.2 WHAT IS NOT A FERROELECTRIC?

All three types of electret – ferroelectric [4], metastable dipole [6], and space-charge [6] – can exhibit similar phenomenology, such as charge or current hysteresis loops [4, 19], or reversible pyroelectric and piezoelectric response [6]. Dipolar electrets, for example, can be polarized artificially with an external electric field [1, 2]. This phenomenon is usually observed in amorphous or glassy systems containing molecular dipoles or polar micro- and nanocrystals that have sufficient rotational mobility at temperatures above the softening point or glass transition temperature, and negligible rotational mobility at lower temperatures. The dipoles can be aligned by applying an electric field above the softening point and frozen in place by cooling in the presence of the field. This type of polar electret can be stable for years and has many uses, including piezoelectric transducers, pyroelectric sensors and imaging arrays, and electro-optic modulators [20].

Amorphous materials, however, cannot be ferroelectric, although they are often mistaken as such. Such reports typically misinterpret one or both of the following observations. Samples may exhibit a pronounced surface charge in displacement as the voltage is cycled, and apparent polarization-field hysteresis loops. But, as mentioned above, this is common behavior in electrets, whether from lagging polarization, charge injection, or space charge accumulation. Such reports often include claims of remanent polarization much larger than the dipole density [21, 22], and are therefore inconsistent with a purely dipolar mechanism. There may be a pronounced dielectric peak as the temperature is increased or decreased. Prior experience has shown [4]

that nearly all inorganic materials exhibiting a dielectric anomaly between two crystalline phases, so-called Curie-Weiss behavior, are ferroelectric in at least one of those phases. This is a misleading indicator in the case of glassy systems, which undergo a quasi-phase-transition where some form of molecular motion is freed up over a range of temperatures. Glass transitions within polar systems, such as polar polymers, will often exhibit a strong dielectric anomaly connected with this motion. It is not, however, related to a ferroelectric phase or phase transition.

Even crystals that have the requisite polar crystal symmetry are not necessarily ferroelectric. Reversibility of the polarization is an essential requirement, which rules out materials that are merely pyroelectric, materials that do have a permanent polarization, but for some reason, often steric hindrance, the electric dipoles cannot all be reversed. This distinction is illustrated in Figure 2. If the molecular dipoles are compact, as are sodium nitrite [14] and thiourea [15, 16], then each molecule is able to rotate in place with minimal disturbance of its neighbors, as indicated by the dashed circle in Figure 2a. Therefore, the polarization is readily transformed between opposite directions and the crystal is ferroelectric. In Figure 2b, the molecules are quite elongated compared to their separation. They cannot rotate in place without interfering with each other (i.e., they are constrained by steric hindrance) and so collective reversal would require prohibitively large strain. This is the case with a large and important class of nonlinear optical molecular crystals [23, 24], many of which are grown from long polar moieties, such as 2-methyl-4-nitroaniline [25]. Designing such molecular pyroelectric crystals is, however, not easy because they typically crystallize with antiparallel dipole moments [23, 24].

The only way to switch the equilibrium polarization state in a sterically hindered crystal, besides the trivial trick of rotating the crystal by 180°, is to take it apart, rearrange the molecules, and put it back together. Therefore, such crystals are merely pyroelectric – there is no continuous path between opposite polarization states.


(a)   **(b)**
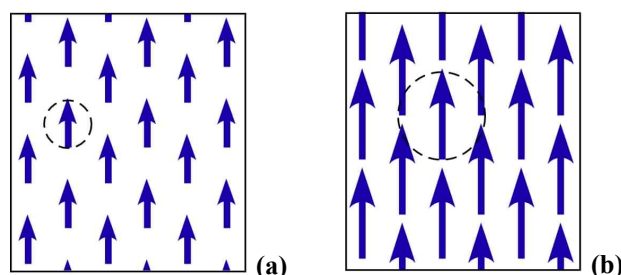
Figure 2. Two polar crystals composed of (a) compact electric dipoles; (b) long electric dipoles;

The prototypical displacive ferroelectric, barium titanate [4], reverses polarization readily because the barium ion has plenty of room to shuttle between two positions toward either end of its tetragonal unit cell. The polarization of gallium nitride [26], on the other hand, arises from the wurtzite structure where the gallium atoms are covalently bonded to one side of a plane of nitrogen atoms. To reverse the polarization direction, the gallium atoms must moved through tightly packed plane of nitrogen atoms, but there is not enough room.

2 POLYVINYLIDENE FLUORIDE

Since the discovery of piezoelectricity in polyvinylidene fluoride (PVDF, -CH_2-CF_2-, **Figure 3**) [27], ferroelectricity has been found in only a small number of crystalline polymers. (We exclude here ferroelectric polymer liquid crystals, where polarization is only a secondary order parameter, although they have much practical value [28].) PVDF stands out because of its highly compact structure and large permanent dipole moment. PVDF, like poly(tetrafluoroethylene) is chemically stable, a major advantage compared to many ferroelectric materials. Nearly any variation in structure adversely affects chemical stability, crystallinity, or rotational mobility, and therefore inhibits ferroelectricity.
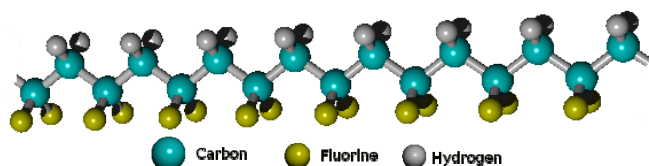

Figure 3. All-trans conformation of PVDF with a coplanar carbon backbone.

The observation in PVDF of piezoelectricity [27], pyroelectricity [29], and even apparent polarization hysteresis [30], were together suggestive of ferroelectricity, but many scientists remained skeptical because the crystallinity was low and there were other mechanisms that could account for these observations [29, 31]. Typical samples of PVDF are polymorphous, containing amorphous material and one or more crystalline phases. One of the crystalline phases, the β phase, has polymer chains of all-trans conformation (**Figure 3**) tightly packed in a quasi-hexagonal polar C_{2V} structure (**Figure 4**a) consistent with ferroelectricity. Because the β phase is a minority phase in PVDF, it was not clear whether or not the observed properties originated in the β phase crystals. Further, there was no apparent ferroelectric to paraelectric phase transition – no Curie-Weiss type dielectric peak between crystalline phases. There is only the melting transition at 170 °C [32]. Although many good arguments were made in favor of the existence of ferroelectricity in PVDF, perhaps the most cogent were made by Kepler and Anderson [33].
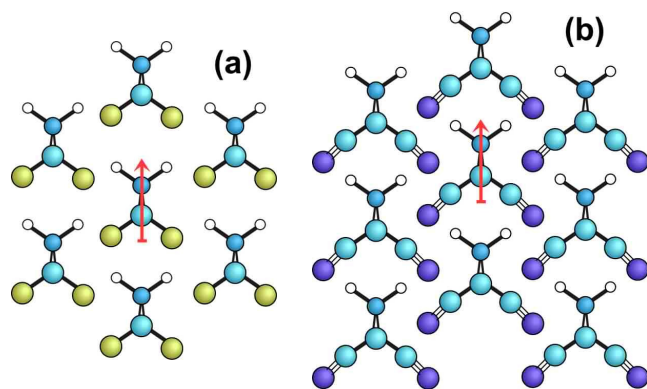
The key to verifying the ferroelectric nature of PVDF was the focus on VDF copolymers with trifluoroethylene (TrFE) [34], which do undergo a clear ferroelectric-paraelectric phase transition and in which ferroelectric polarization hysteresis is characteristic only of the lower temperature phase [35]. Copolymers of VDF with TrFE or with tetrafluoroethylene (TeFE) have binary phase diagrams where the melting point and ferroelectric-paraelectric phase transition temperature vary smoothly with composition [36]. In the case of VDF-TrFE copolymers, the melting point dips to a minimum at about 80% VDF, but the transition temperature decreases monotonically with addition of either TrFE or TeFE due mainly to the disorder of the random copolymer [36-40]. Consequently, below about 85% VDF, the transition temperature is below the melting point, and copolymers in this range afford the most comprehensive study of the full range of ferroelectric and related properties. (It turns out that an equilibrium ferroelectric phase transition temperature extrapolates to well above the material's melting point, as was determined from the effect of pressure on the transition temperature [37].) The emergence of this evidence, a decade after the discovery of piezoelectricity in PVDF [27], initiated intensive study of ferroelectric polymers [32, 41]. Although the ferroelectric copolymers of VDF with TrFE and TeFE have slightly reduced spontaneous polarization, because some of the hydrogen atoms are replaced with fluorine atoms, their main advantage is that they can be annealed to nearly 100% crystallinity, whereas pure PVDF is typically limited to 50% crystallinity even with extensive annealing, stretching, and poling treatments [41]. Increasing the disorder by, for example, electron radiation [42, 43] or making a terpolymer of VDF and TrFE with 5% to 10% CTFE suppresses ferroelectricity and tends to produce polymorphous relaxors with exceptionally large electrostrictive and dielectric responses [44-47]. Terpolymers of VDF and TrFE with 9% hexafluroacetone [48] or with up to 6% hexafluorpropylene [49] show similar disorder effects suppressing ferroelectricity.
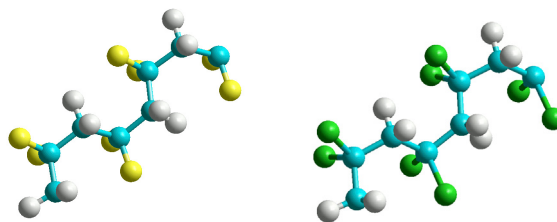
Figure 5. Trans-gauche conformations of PVDF (left) and PVDC (right). (Regular structures shown – actual structures may have random helicity.)

It seems that PVDF has the ideal molecular structure for a ferroelectric polymer. The electronegative fluorines contribute to a large net dipole moment (about 2 Debye) per –CF_2–CH_2– monomer perpendicular to the backbone. The dipoles are conveniently strung in a compact nearly cylindrical rod polymer, which in the ferroelectric phase has a planar all-trans conformation (**Figure 3**) arranged in a quasi-hexagonal close-packed crystal structure (**Figure 4**a). This structure has a nominal dipole density of 0.13 C/m^2, which is close to the experimentally determined value of approximately 0.11 C/m^2 [32]. *Ab initio* calculations indicate that the actual polarization

Figure 4. Crystal structure of all-trans β phase crystals, viewed along the polymer chains, of: **(a)** PVDF and **(b)** PVDCN showing the relative sizes and crystal packing. The arrows show the direction of the net molecular dipole moments.

should be somewhat larger, about 0.18 C/m^2, due to local field (Lorentz) corrections [50]. For comparison, barium titanate has a polarization of 0.26 C/m^2 [4]. The compact molecular cross-section and ease of formation of gauche bonds provide the essential mechanism responsible for both switching by gauche kink propagation [51] and for the transition between the all-trans (**Figure 3**) and alternating trans-gauche (**Figure 5**a) conformations constituting ferroelectric and paraelectric phases [52], respectively. For these reasons, the VDF copolymers are by far the most extensively studied ferroelectric polymers.

3   OTHER FERROELECTRIC POLYMERS

Can other ferroelectric polymers match or exceed the properties of PVDF and its copolymers? One of the first reported alternatives to PVDF is the odd nylon system, which consists of a planar –CH$_2$– backbone with polar carbonyl –C=O dipoles sticking out of the same side of the chain. The odd nylons [53-58], which have all the carbonyl groups on the same side of the molecule, are indeed ferroelectric, with polarizations increasing with carbonyl content, ranging from 40 mC/m^2 to 130 mC/m^2 [56], which is comparable to the range for PVDF and its copolymers. The odd nylons are inexpensive and easy to process and make good piezoelectric [53-55] and pyroelectric [53, 57, 59] materials. Polarization switching, however, is hindered by hydrogen bonding between the =O and CH$_2$ on neighboring chains, making these materials difficult to polarize or switch.

A simpler and more direct approach is to break the symmetry of the backbone by replacing the carbons with boron and nitrogen to form the polyethylene analog polyaminoborane [60], –BH$_2$–NH$_2$–, or the PVDF analog, polyaminodifluoroborane [61], –BF$_2$–NH$_2$–. *Ab initio* calculations confirm this advantage, yielding polarizations of 0.30 C/m^2 and 0.36 C/m^2 for polyaminoborane and polyaminodifluoroborane, respectively [50]. These polymers are much more chemically reactive than PVDF and, to our knowledge, there are no published reports of ferroelectric or related properties of these polymers.

A relatively simple analog of PVDF is obtained by substitution of chlorine atoms for the fluorine atoms. Because chlorine is less electronegative (3.16 on the Pauling scale) than fluorine (3.98), this would reduce the dipole moment, and therefore the polarization, of a ferroelectric form. But even more important, the larger covalent radius of chlorine (1.0 Å vs. 0.7 Å for fluorine) makes the all-trans conformation completely unstable. The fluorines in PVDF (and PTFE as well) are already slightly too large for the planar all-trans conformation, resulting in a small dihedral tilt in the backbone. The much larger chlorine atoms, therefore, destabilize the all-trans structure necessary for the ferroelectric phase, and so polyvinylidene chloride (PVDC, -CH$_2$-CCl$_2$-), for example, supports only the trans-gauche conformation (see **Figure 5**b) characteristic of the paraelectric phase of PVDF [62] and its copolymers with TrFE [63]. Here, the vinyl chloride likely serves to break up sequences of trans bond conformation, thus inhibiting ferroelectricity while retaining many short trains of trans bonds that follow the electric field collectively. Polyvinyl chloride

(PVC), forms a polar all-trans molecular structure of the form -CH$_2$-CHCl-CH$_2$-CClH- where the chlorine atoms alternate left and right. It doesn't crystallize well, and appears to have a nonpolar structure when it does [64]. PVC is readily stretched and poled to make an electret with good piezoelectric and pyroelectric properties [10, 65], more so with plasticizer added [66]. Claims that PVC is ferroelectric, however, are based on poorly formed hysteresis loops that better resemble electret behavior [67].

4   CYANOPOLYMERS

Because of the large dipole moment associated with the cyano group (–C≡N) of approximately 3.5 debye compared to 2 debye for VDF [11], it is a promising candidate for chemical replacement in the development of highly polar, and potentially ferroelectric, polymer analogs to PVDF. Further, the cyano groups are slim enough that they don't destabilize the all-trans conformation. The most direct cyanopolymer analog is PVDCN (**Figure 4**b), in which all of the electronegative fluorine atoms of PVDF are replaced by –C≡N [68-70]. Unfortunately, because of the highly reactive nature of the VDCN monomer, the PVDCN homopolymer has proven to be unstable in ambient conditions, decomposing readily in the presence of water. A relatively minor modification is to add methyl groups, as in poly methyl vinylidene cyanide (PMVC, **Figure 6**). This addition reduces polymer reactivity and results in a slightly amphiphilic character suitable for Langmuir-Blodgett (LB) deposition, a method that proved useful for making ultrathin films of VDF copolymers [71-73]. The PMVC version should result in better quality LB films due to its stronger amphiphilic character, and that proved to be the case. PMVC exhibited much more ideal pressure-area isotherms on the LB trough, and resulted in better LB films that didn't require annealing as do the VDF copolymer LB films [74]. Like PVDF, PMVC has the and all-trans conformation polar crystal structure, stable pyroelectric response, and dielectric hysteresis [75]. The polarization is readily reversed well below the melting point and is stable for days [74]. Also like PVDF, PMVC reveals no phase transition below the melting point, and therefore polarization hysteresis and stability alone are not definitive evidence of ferroelectricity. Therefore it seems appropriate to follow the successful example of the VDF copolymers by investigating cyano copolymers.

Because VDCN is so reactive [11], it readily forms regular alternating polymers with other monomers [68, 69, 76]. This regular alternation behavior is in contrast to the VDF copolymers [37, 77], in which the TrFE or TeFE monomers appear to form random copolymers with PVDF [36]. One example is the alkyl fatty acid esters, which have a variable length of *n* alkyl spacers [68, 78], which affords additional synthetic flexibility. The most extensively studied of these is the *n* = 2 fatty acid or poly(vinylidene cyanide-vinyl acetate), P(VDCN-VAC) shown in **Figure 6** [68-70]. Solvent-cast samples of the P(VDCN-VAC) 50:50 copolymer had relatively low crystallinity, according to x-ray diffraction studies [69]. Our x-ray

diffraction measurements carried out on powder samples of P(VDCN-VAC) 50:50, qualitatively verify these observations [75]. In both cases, the measurements indicate broad theta-2theta x-ray reflections at approximately 2θ=15° and 2θ=30°, an observation consistent with the presence of polymer crystallites with an average diameter of approximately 20 Å, calculated using the Debye-Scherrer equation, and a *d*-spacing of approximately 5.9 Å. Clearly, the relatively small crystallite size would limit the long range order in the P(VDCN-VAC) system and suggests the thick cast samples of the cyanopolymer are indeed polymorphous in nature, with small crystallites embedded in an amorphous matrix. The low crystallinity inferred from the x-ray diffraction results is consistent with the lack of a clear crystal melting peak in differential scanning calorimetry (DSC) measurements [68, 69]. The DSC measurements did, however, show a large exothermic peak at 170 °C on heating, indicating a glass transition [68]. It has been suggested [69, 76] that the highly polar –C≡N side groups form dipole-dipole bonds within 3 or 4 neighboring chains, creating a paracrystal [13], which consists of small aggregates of tightly packed and aligned cyanopolymer chains. This aggregation of polymer chains, it was suggested, allows for the cooperative polarization reversal in the presence of a sufficiently large bias field [10, 68, 69].
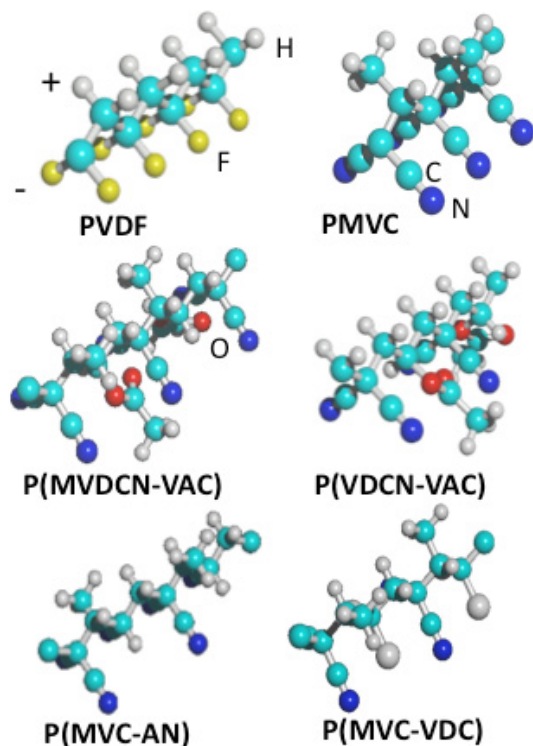
[4]. They have attributed this peak to "ferroelectric glass" behavior. Because the P(VDCN-VAC) copolymer has two monomers that both possess relatively large side chains, it is reasonable that the anomaly observed above the onset of the glass transition is simply the activation of one or both of these side groups, allowing them to more freely respond to the applied field. The material under study, however, was reported to be amorphous, which is inconsistent with ferroelectricity.

Another system that has proven fruitful in the study of ferroelectricity and electroactivity in cyanopolymers is that of polyacrylonitrile, PAN [79-81]. Although similar to PVDCN, PAN has only one cyano group per monomer, with the missing –C≡N group replaced by a single hydrogen atom, as shown in Figure 7a. As a result, the PAN monomer has a reduced polarization compared to a PVDCN. One advantage that PAN has over PVDCN is that the PAN homopolymer is quite stable in ambient conditions [79, 80], therefore permitting detailed study of the homopolymer's electroactive properties.
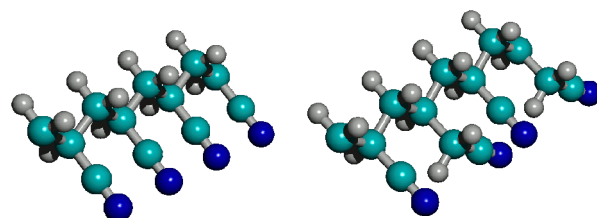

Figure 7. Chemical structure of an acrylonitrile homopolymer (PAN, left) and its copolymer with allycyanide, P(AN-AL).

Studies of PAN include piezoelectric and pyroelectric response [80, 82], dielectric constant [83], and crystal structure [81]. Structural studies performed with x-ray diffraction and NMR [81] indicate that the PAN homopolymer packs in a pseudohexagonal manner with the predominantly planar zig-zag chain conformation, analogous to the conformation in the all-trans ferroelectric β-phase found in PVDF. In addition, it has been shown that along the PAN chain exist randomly spaced kinks, resulting in a relatively large degree of disorder, perhaps similar to a disordered version of the γ phase found in PVDF, where there are about 25% gauche bonds (compared to 0% in the ferroelectric phase and 50% in the paraelectric phase). The proposed packing model is that of a hexagonal arrangement of rigid rods [81]. Additionally, XRD measurements of cast samples show a strong dependence of the intensity of the x-ray reflection on the strength of the poling electric field used to prepare the system [79]. These measurements were performed at 145 °C with various electric field strengths. The results clearly show that at a field of 5 MV/m and temperature 145 °C the diffraction line associated with a 5.2 Å crystal *d*-spacing begins to narrow, indicating an increase in average crystallite size. It is reasonable that application of a large electric field aids in the alignment of monomer dipoles, which suffer from the disorder caused by the random kinking down the polymer chain, and thus helping to stabilize a polar phase. Liu and Roland [81] found no evidence for the coexistence of multiple phases, as is the case in untreated cast PVDF films, in which polymorphous films possess regions of

Figure 6. Structures of PVDF and five cyanopolymer analogs.

Dielectric studies of the non-methylated copolymer P(VDCN-VAC) 50:50 [76] showed no dielectric anomaly below the 170 °C glass transition temperature. At temperatures well above the onset of the glass transition, at approximately 210 °C, there is rise in capacitance that Wang et al. [76] call "ferroelectriclike" due to it's similarity to Curie-Weiss behavior

both all-trans and trans-gauche conformation [81, 84]. Further, piezoelectric studies have shown that stretching PAN fibers results increases the piezoelectric response, which, again, is consistent with the "unkinking" of the polymer chains (removing gauche bonds) due to strain. Ueda et al. [80] found evidence for unkinking by an external electric field. Because of the semi-crystalline character of PAN, it exhibits both a glass transition and a crystalline melting point, which occur at approximately 85° C and 320° C, respectively [21]. The strength and position of the glass transition in PAN is highly dependent upon sample history, as suggested by the increase of crystallinity under the influence of an electric field at elevated temperature [79].

Although PAN has proven an interesting system to study, a large amount of work pertaining to the acrylonitrile system has focused on the copolymer system poly(acrylonitrile-allylcyanide) [21, 82], or P(AN-AL), which is shown in Figure 7b. The introduction of the co-monomer into the PAN structure appears to increase the internal mobility of the monomers [21]. As a result of this increased mobility, the interaction between neighboring cyano groups is reduced sufficiently to help stabilize the structure against gauche bond (kink) formation, which was prevalent in PAN. The reduced kinking increases the length of trans bond sequences and therefore promotes long range conformational order and produces larger crystallites. The width of the x-ray diffraction peak at 5.2 Å exhibits a marked narrowing, indicating an increase in crystal size [21]. This *d*-spacing is significantly more compact than the 5.9 Å spacing measured in P(VDCN-VAC) [68], where the relatively broad peak indicates lower crystal coherence. It appears that by copolymerizing the allyl-cyanide with the smaller acrylonitrile affords more rotational freedom, helping to prevent kinks, while at the same time keeping adjacent chains relatively close-packed, resulting in increased crystallinity.

Although the P(AN-AL) copolymer has improved crystallinity compared to PAN, it is still highly polymorphic, with a rather small crystallinity. Electrical measurements of cast films of 65:35 P(AN-AL) resulted in an unreasonably large polarization hysteresis of 700 mC/m^2 [21]. This is much larger than the polarization found in P(VDF-TrFE) copolymers, whether measured (50-130 mC/m^2) or calculated from first principles (100-180 mC/m^2). The apparent polarization reported for P(AN-AL) is almost certainly too large to attribute solely to the permanent dipoles, and is likely an experimental artifact that is caused by conduction or charge injection. Moreover, the experiment was performed at 105 °C, which is approximately 15 °C above the reported glass transition temperature of 90 °C [21]. Again, at temperatures above T_g, dielectric hysteresis cannot be related to ferroelectricity because the material lacks the requisite crystalline symmetry. As the temperature was lowered, observation of charge hysteresis required much higher fields until, below 68 °C, switching was no longer observed. Most critically the samples depolarized rapidly when the bias field was removed [21], indicating that the polarization quickly relaxed like a poor electret, exhibiting metastable dipolar alignment or charge injection.

The evidence offered for the existence of ferroelectricity in P(VDCN-VAC), PAN, or P(AN-AL), appears weak under close scrutiny. Rather, it appears that the reported charge hysteresis and dielectric anomalies can all be attributed to metastable electret effects. This does not, however, rule out the existence of ferroelectricity in these, or other cyanopolymer systems. With improved experimental techniques and close attention to the contribution of the apparent polarization reversal, it may be possible to delimit the existence or non-existence of ferroelectricity in these and related systems.

5   SUMMARY

Polyvinylidene fluoride is indeed special, primarily because of its compact linear molecular structure and supple backbone. Changing the structure adversely affects these qualities in the analogs studied thus far. Increasing disorder by inserting, for example TrFE, TeFE, or CTFE reduces the transition temperature or converts the system to relaxor behavior. The odd nylons and odd polyureas have reduced backbone flexibility, and inhibiting hydrogen bonds, making them hard to switch. Halogen substitution with anything larger than fluorine destabilizes the all-trans structure. Replacing the fluorines with cyano groups retains the all-trans structure, but in a close-packed crystal, they encounter steric hindrance that inhibits polarization switching. The boron nitride backbone, with or without fluorines, is predicted to have approximately twice the polarization of PVDF, and is perhaps the most promising analog to investigate.

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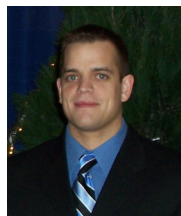
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