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Piezoelectric Polymers

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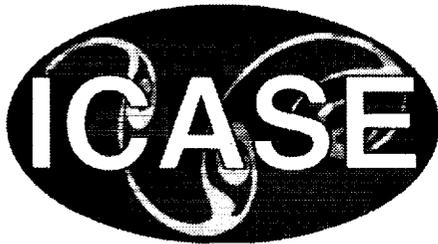
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PIEZOELECTRIC POLYMERS

J. S. HARRISON¹ AND Z. OUNAIES²

Abstract. The purpose of this review is to detail the current theoretical understanding of the origin of piezoelectric and ferroelectric phenomena in polymers; to present the state-of-the-art in piezoelectric polymers and emerging material systems that exhibit promising properties; and to discuss key characterization methods, fundamental modeling approaches, and applications of piezoelectric polymers. Piezoelectric polymers have been known to exist for more than forty years, but in recent years they have gained notoriety as a valuable class of smart materials.

Key words. piezoelectricity, amorphous polymers, semicrystalline polymers, ferroelectricity, piezoelectric coefficient, hysteresis, dipole orientation, poling, modeling, piezoelectric characterization

Subject classification. Structures and Materials: Materials

1. Introduction.

1.1. Basic Definitions. Upon reviewing the abundance of literature on the subject, it is clear that there is no standard definition for smart materials, and that terms such as intelligent materials, smart materials, adaptive materials, active devices, and smart systems, are often used interchangeably. The term *smart material* generally designates a material that changes one or more of its properties in response to an external stimulus.

The most popular smart material systems are piezoelectric materials, magnetostrictive materials, shape memory alloys, electrorheological fluids, electrostrictive materials and optical fibers. Magnetostrictives, electrostrictives, shape memory alloys and electrorheological fluids are used as actuators while optical fibers are used primarily as sensors.

Among these active materials, piezoelectric materials are most widely used because of their wide bandwidth, fast electromechanical response, relatively low power requirements and high generative forces. A classical definition of piezoelectricity, a Greek term for *pressure electricity*, is the generation of electrical polarization in a material in response to a mechanical stress. This phenomenon is known as the direct effect. Piezoelectric materials also display the converse effect; mechanical deformation upon application of electrical charge or signal. Piezoelectricity is a property of many non-centrosymmetric ceramics, polymers and other biological systems. A subset of piezoelectricity is pyroelectricity, whereby the polarization is a function of temperature. Some pyroelectric materials are ferroelectric, although not all ferroelectrics are pyroelectric. Ferroelectricity is a property of certain dielectrics, which exhibit a spontaneous electric polarization (separation of the center of positive and negative electric charge, making one side of the crystal positive and the opposite side negative) that can be reversed in direction by the application of an appropriate electric field. Ferroelectricity is named by analogy with ferromagnetism, which occurs in materials such as iron. Traditionally, ferroelectricity is defined for crystalline materials, or at least in the crystalline region of semicrystalline materials. In the last couple of years, however, a number of researchers have explored the possibility of ferroelectricity in amorphous polymers, i.e., ferroelectricity without the crystal lattice structure (1).

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1.2. Characteristics of Piezoelectric Polymers. The properties of polymers are so different in comparison to inorganics (Table 1) that they are uniquely qualified to fill niche areas where single crystals and ceramics are incapable of performing as effectively. As noted in Table 1, the piezoelectric strain constant (d_{31}) for the polymer is lower than that of the ceramic. However, piezoelectric polymers have much higher piezoelectric stress constants (g_{31}) indicating that they are much better sensors than ceramics. Piezoelectric polymeric sensors and actuators offer the advantage of processing flexibility because they are lightweight, tough, readily manufactured into large areas, and can be cut and formed into complex shapes. Polymers also exhibit high strength and high impact resistance (2). Other notable features of polymers are low dielectric constant, low elastic stiffness, and low density, which result in a high voltage sensitivity (excellent sensor characteristic), and low acoustic and mechanical impedance (crucial for medical and underwater applications). Polymers also typically possess a high dielectric breakdown and high operating field strength, which means that they can withstand much higher driving fields than ceramics. Polymers offer the ability to pattern electrodes on the film surface, and pole only selected regions. Based on these features, piezoelectric polymers possess their own established area for technical applications and useful device configurations.

TABLE I.
Property comparison for standard piezoelectric polymer and ceramic materials

	d_{31}^a (pm/V)	g_{31}^a (mV-m/N)	k_{31}	Salient Features
Polyvinylidene fluoride (PVDF)	28	240	0.12	flexible, lightweight, low acoustic and mechanical impedance
Lead Zirconium Titanate (PZT)	175	11	0.34	brittle, heavy, toxic

^a Values shown are absolute values of constants.

2. Structural Requirements for Piezoelectric Polymers. The following sections explain piezoelectric mechanisms for both semicrystalline and amorphous polymers. Although there are distinct differences, particularly with respect to polarization stability, in the simplest terms, four critical elements exist for all piezoelectric polymers, regardless of morphology. As summarized by Broadhurst and Davis (3) these essential elements are: (a) the presence of permanent molecular dipoles; (b) the ability to orient or align the molecular dipoles; (c) the ability to sustain this dipole alignment once it is achieved; and (d) the ability of the material to undergo large strains when mechanically stressed.

2.1. Semicrystalline Polymers.

2.1.1. Mechanism of piezoelectricity in semicrystalline polymers. In order to render them piezoelectric, semicrystalline polymers must have a polar crystalline phase. The morphology of such polymers consists of crystallites dispersed within amorphous regions as shown in Figure 1a. The amorphous region has a glass transition temperature that dictates the mechanical properties of the polymer while the crystallites have a melting temperature that dictates the upper limit of the use temperature. The degree of crystallinity present in such polymers depends on their method of preparation and thermal history. Most semicrystalline polymers have several polymorphic phases, some of which may be polar. Mechanical orientation, thermal annealing and high voltage treatment have all been shown to be effective in inducing crystalline phase transformations. Stretching the polymer essentially aligns the amorphous strands in the film plane as shown in Figure 1b and facilitates uniform rotation of the crystallites by an

electric field. Depending on whether stretching is uniaxial or biaxial, the electrical and mechanical properties (and therefore the transduction response), are either highly anisotropic or isotropic in the plane of the polymer sheet. Electrical poling is accomplished by applying an electric field across the thickness of the polymer as depicted in Figure 1c. An electric field on the order of 50 MV/m is typically sufficient to effect crystalline orientation. Polymer poling can be accomplished using a direct contact method or a corona discharge. The latter method is advantageous since contacting electrodes are not required and large area samples can be poled in a continuous fashion. This method is used to manufacture commercially available polyvinylidene fluoride (PVDF) film. Some researchers have also successfully poled large area polymer films by sandwiching films between polished metal plates under a vacuum. This method essentially eliminates electrical arcing of samples and the need for depositing metal electrodes on the film surface. For semicrystalline polymers the amorphous phase supports the crystal orientation and the polarization is stable up to the Curie temperature. This polarization can remain constant for many years if it is not influenced by the spurious effects of moisture uptake or elevated temperatures.

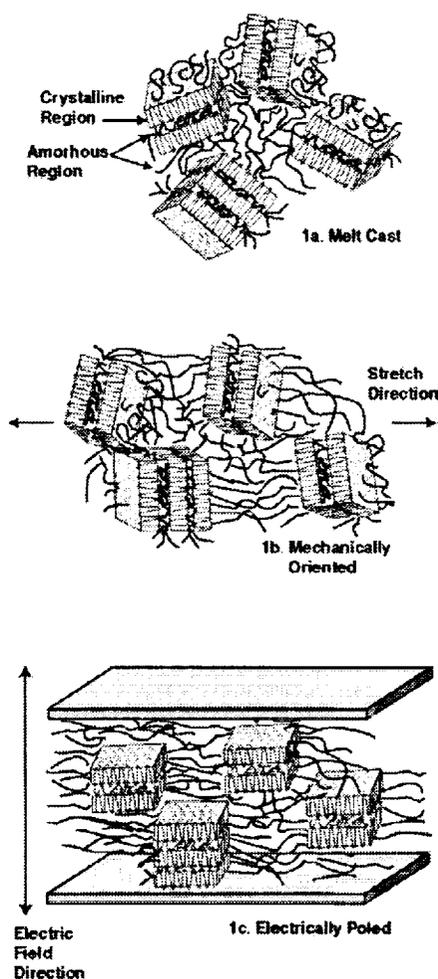


FIG. 1. Schematic illustration showing random stacks of amorphous and crystal lamellae in PVDF polymer. Figure (1a) represents the morphology after the film is melt cast; (1b) is after orientation of the film by mechanically stretching to several times its original length; (1c) is after depositing metal electrodes and poling through the film thickness.

2.1.2. Piezoelectric constitutive relationships. The constitutive relations describing the piezoelectric behavior in materials can be derived from thermodynamic principles (4). A tensor notation is adopted to identify the coupling between the various entities through the mechanical and electrical coefficients. The common practice is to label directions as depicted in Figure 2. The stretch direction is denoted as “1”. The “2” axis is orthogonal to the stretch direction in the plane of the film. The polarization axis (perpendicular to the surface of the film) is denoted as “3”. The shear planes are indicated by the subscripts “4”, “5”, “6” and are perpendicular to the directions “1”, “2”, and “3” respectively. By reducing the tensor elements and using standard notations (5), the resulting equations can be displayed in matrix form as follows

$$\begin{pmatrix} S_1 \\ S_2 \\ S_3 \\ S_4 \\ S_5 \\ S_6 \end{pmatrix} = \begin{pmatrix} d_{11} & d_{12} & d_{13} \\ d_{21} & d_{22} & d_{23} \\ d_{31} & d_{32} & d_{33} \\ d_{41} & d_{42} & d_{43} \\ d_{51} & d_{52} & d_{53} \\ d_{61} & d_{62} & d_{63} \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} + \begin{pmatrix} s_{11}^E & s_{12}^E & s_{13}^E & s_{14}^E & s_{15}^E & s_{16}^E \\ s_{21}^E & s_{22}^E & s_{23}^E & s_{24}^E & s_{25}^E & s_{26}^E \\ s_{31}^E & s_{32}^E & s_{33}^E & s_{34}^E & s_{35}^E & s_{36}^E \\ s_{41}^E & s_{42}^E & s_{43}^E & s_{44}^E & s_{45}^E & s_{46}^E \\ s_{51}^E & s_{52}^E & s_{53}^E & s_{54}^E & s_{55}^E & s_{56}^E \\ s_{61}^E & s_{62}^E & s_{63}^E & s_{64}^E & s_{65}^E & s_{66}^E \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix} \quad (1)$$

$$\begin{pmatrix} D_1 \\ D_2 \\ D_3 \end{pmatrix} = \begin{pmatrix} \epsilon_{11}^T & \epsilon_{12}^T & \epsilon_{13}^T \\ \epsilon_{21}^T & \epsilon_{22}^T & \epsilon_{23}^T \\ \epsilon_{31}^T & \epsilon_{32}^T & \epsilon_{33}^T \end{pmatrix} \begin{pmatrix} E_1 \\ E_2 \\ E_3 \end{pmatrix} + \begin{pmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{pmatrix} \begin{pmatrix} X_1 \\ X_2 \\ X_3 \\ X_4 \\ X_5 \\ X_6 \end{pmatrix} \quad (2)$$

Piezoelectricity is a cross coupling between the elastic variables, stress X and strain S , and the dielectric variables, electric charge density D and electric field E . It is noted that D is named in analogy to the B -field in ferromagnetism although some authors also refer to it as dielectric or electric displacement. There does not seem to be a standard nomenclature, however, it is the opinion of the authors of this chapter that electric charge density is a better description of this property. The combinations of these variables define the piezoelectric strain constant d , the material compliance s and the permittivity ϵ . Other piezoelectric properties are the piezoelectric voltage constant g , stress constant e and strain constant h given by equations in Table 2. For a given constant, the first definition in the table refers to the direct effect while the second one refers to the converse effect. The piezoelectric constants are interrelated through the electrical and mechanical properties of the material. Electric field strength and electric

charge density are related through the dielectric constant, $\epsilon\epsilon$ (where ϵ is the permittivity of free space), while stress and strain are related through the compliance according to

$$d_{ij} = \epsilon_0 \epsilon_i g_{ij} \quad (3)$$

$$e_{ij} = s_{ij} d_{ij} \quad (4)$$

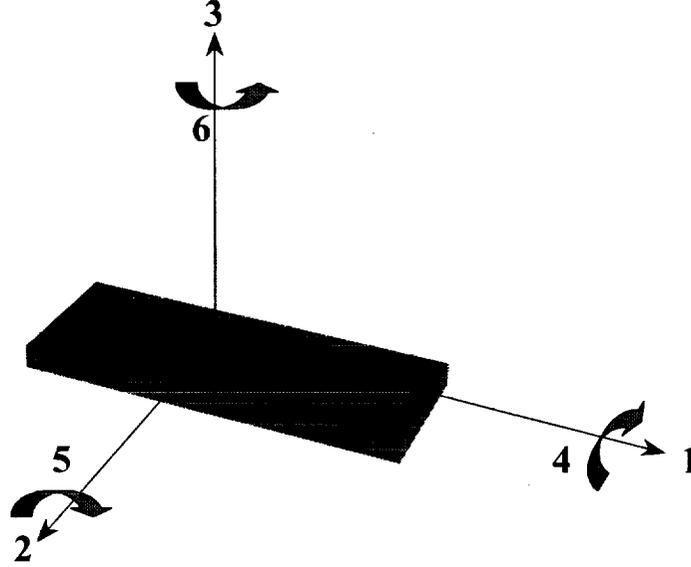


FIG. 2. Tensor directions for defining the constitutive relations

The polarization P is a measure of the degree of piezoelectricity in a given material. In a piezoelectric material, a change in polarization ΔP results from an applied stress X or strain S under the conditions of constant temperature and zero electric field. A linear relationship exists between ΔP and the piezoelectric constants. Due to material anisotropy, P is a vector with three orthogonal components in the 1, 2, and 3 directions. Alternatively, the piezoelectric constants can be defined as

$$\Delta P_i = d_{ij} X_j \quad (5)$$

$$\Delta P_i = g_{ij} S_j \quad (6)$$

The electrical response of a piezoelectric material is a function of the electrode configuration relative to the direction of the applied mechanical stress. For a coefficient, d_{ij} , the first subscript is the direction of the electric field or charge displacement while the second subscript gives the direction of the mechanical deformation or stress. The C_2 crystallographic symmetry typical of synthetic oriented, poled polymer film leads to the cancellation of all but five of the d_{ij} components (d_{31} , d_{32} , d_{33} , d_{15} and d_{24}). If the film is poled and biaxially oriented or unoriented, $d_{3j} = d_{32}$ and $d_{15} = d_{24}$. Most natural biopolymers possess D_∞ symmetry which yields a matrix possessing only the shear piezoelectricity components d_{13} and d_{25} . Since the d_{33} constant is difficult to measure without constraining the

sample in its lateral dimension, it is typically determined from Equation 7 which relates the constants to the hydrostatic piezoelectric constant, d_{3h} .

$$d_{3h} = d_{31} + d_{32} + d_{33} \quad (7)$$

TABLE 2.
Definitions for piezoelectric constants.

Equations	Units
$d = (dD/dX)_E = (dS/dE)_X$	(C/N or m/V)
$e = (dD/dS)_E = -(dX/dE)_S$	(C/m or N/Vm)
$g = (dE/dX)_D = (dS/dD)_X$	(Vm/N or m ² /C)
$h = (dE/dS)_D = -(dX/dD)_S$	(V/m or N/C)

The electromechanical coupling coefficient k_{ij} represents the conversion of electrical energy into mechanical energy and vice versa. The electromechanical coupling can be considered as a measure of transduction efficiency and is always less than unity as shown below

$$k^2 = \frac{\text{electrical energy converted to mechanical energy}}{\text{input electrical energy}} \quad (8a)$$

$$k^2 = \frac{\text{mechanical energy converted to electrical energy}}{\text{input mechanical energy}} \quad (8b)$$

Some k coefficients can be obtained from measured d -constant as follows

$$k_{31} = \frac{d_{31}}{\sqrt{S_{11}^E \epsilon_3^T}} \quad (9)$$

2.1.3. Ferroelectricity in semicrystalline polymers. At high electric fields, the polarization that occurs in semicrystalline polymers such as PVDF is nonlinear with the applied electric field. This nonlinearity in polarization is defined as hysteresis. The existence of a spontaneous polarization together with polarization reversal (as illustrated by a hysteresis loop) is generally accepted as proof of ferroelectricity. Figure 3 is an example of the typical hysteresis behavior of PVDF. Two other key properties typically reported for ferroelectric materials are the coercive field and the remanent polarization. The coercive field, E_c , which marks the point where the hysteresis intersects with the horizontal axis, is typically about 50 MV/m at room temperature for many ferroelectric polymers. The remanent polarization, P_r , corresponds to the point where the loop intersects with the vertical axis. The values of E_c and P_r are dependent on the temperature and frequency of measurement. The Curie temperature T_c , is generally

lower than but close to the melting temperature of the polymer. Below T_c , the polymer is ferroelectric and above T_c , the polymer loses its non-centrosymmetric nature.

Although ferroelectric phenomenon has been well documented in ceramic crystals, the question of whether polymer crystallites could exhibit dipole switching was debatable for about a decade following the discovery of piezoelectricity in PVDF. Inhomogeneous polarization through the film thickness which yielded higher polarization on the positive electrode side of the polymer led to speculations that PVDF was simply a trapped charge electret. These speculations were dispelled when X-ray studies (6) demonstrated that polarization anisotropy vanishes with high poling field strengths and that true ferroelectric dipole reorientation occurs in PVDF. Luongo used infrared to attribute the polarization reversal in PVDF to 180° dipole rotation (7). Scheinbeim has documented the same via X-ray pole analysis and infrared techniques for odd nylons (8).

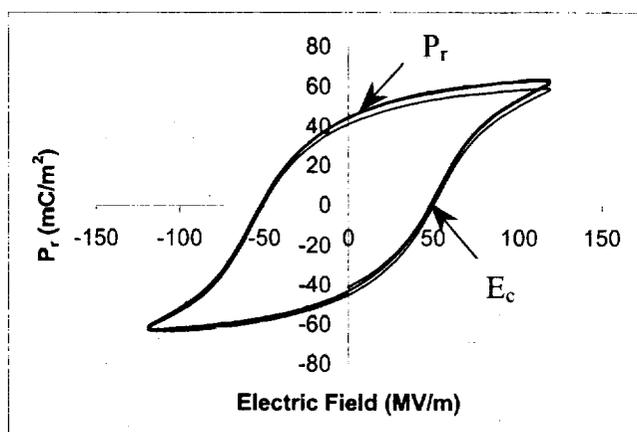
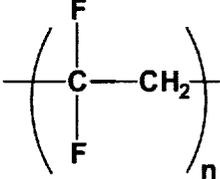
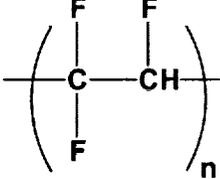
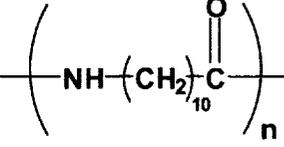
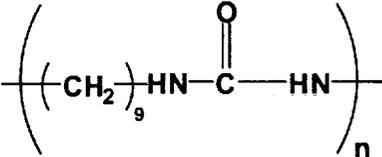


FIG. 3. Typical ferroelectric hysteresis loop for PVDF.

2.1.4. State-of-the-art. Pioneering work in the area of piezoelectric polymers by Kawai (9) has led to the development of strong piezoelectric activity in polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (TrFE) and tetrafluoroethylene (TFE). These semicrystalline fluoropolymers represent the state of the art in piezoelectric polymers and are currently the only commercially available piezoelectric polymers. Odd-numbered nylons, the next most widely investigated semicrystalline piezoelectric polymers, have excellent piezoelectric properties at elevated temperatures but have not yet been embraced in practical application. Other semicrystalline polymers including polyureas, liquid crystalline polymers, biopolymers and an array of blend combinations have been studied for their piezoelectric potential and are summarized in the following section. The chemical repeat unit and piezoelectric constants are depicted in Table 3 for several semicrystalline polymers.

TABLE 3.

Comparison of piezoelectric properties of some semicrystalline polymeric materials.

Polymer	Structure	T _g (°C)	T _m (°C)	Max Use Temp (°C)	d ₃₁ (pC/N)	Ref.
PVDF		-35	175	80	20-28	2
PTrFE		32	150	90-100	12	2
Nylon-11		68	195	185	3 @ 25°C 14 @ 107°C	22
Polyurea-9		50	180	-	-	28

2.1.4.1. Polyvinylidene fluoride (PVDF). Interest in the electrical properties of PVDF began in 1969 when Kawai (9) showed that thin films that had been poled exhibited a very large piezoelectric coefficient, 6-7 pC/N⁻¹, a value which is about ten times larger than had been observed in any other polymer. As seen in Table 3, PVDF is inherently polar. The spatially symmetrical disposition of the hydrogen and fluorine atoms along the polymer chain gives rise to unique polarity effects that influence the electromechanical response, solubility, dielectric properties, crystal morphology and yield an unusually high dielectric constant. The dielectric constant of PVDF is about 12, which is four times greater than most polymers, and makes PVDF attractive for integration into devices as the signal to noise ratio is less for higher dielectric materials. The amorphous phase in PVDF has a glass transition that is well below room temperature (-35°C), hence the material is quite flexible and readily strained at room temperature. PVDF is typically 50 to 60% crystalline depending on thermal and processing history and has at least four crystal phases (α , β , γ , and δ), of which at least three are polar. The most stable, non-polar α phase results upon casting PVDF from the melt and can be transformed into the polar β phase by mechanically stretching

at elevated temperatures or into the polar δ phase by rotating the molecular chain axis with a high electric field (~ 130 MV/m) (10). The β phase is most important for piezoelectric considerations and has a dipole moment perpendicular to the chain axis of 2.1 D corresponding to a dipole concentration of 7×10^{-30} Cm. After poling PVDF, the room temperature polarization stability is excellent, however, polarization and piezoelectricity degrade with increasing temperature and is erased at its Curie temperature. Previously it was believed that polarization stability was defined only by the melting temperature of the PVDF crystals. Recently, however, some researchers suggest that the polarization stability of PVDF and its copolymers is associated with Coulomb interactions between injected, trapped charges and oriented dipoles in the crystals (11). They hypothesize that the thermal decay of the polarization is caused by the thermally activated removal of the trapped charges from the traps at the surface of the crystals. The role of trapped charges in stabilizing orientation in both semicrystalline and amorphous polymers is still a subject that needs further study. The electromechanical properties of PVDF have been widely investigated. For more details, the reader is referred to the wealth of literature that exists on the subjects of the piezoelectric, pyroelectric, and ferroelectric properties (2, 6, 12, 13), and morphology (14-16) of this polymer.

2.1.4.2. Poly(vinylidene fluoride-trifluoroethylene and tetrafluoroethylene) copolymers. Copolymers of polyvinylidene fluoride with trifluoroethylene (TrFE) and tetrafluoroethylene (TFE) have also been shown to exhibit strong piezoelectric, pyroelectric and ferroelectric effects. Here, these polymers are discussed together since they behave similarly when copolymerized with PVDF. An attractive morphological feature of the comonomers is that they force the polymer into an all-trans conformation that has a polar crystalline phase, which eliminates the need for mechanical stretching to yield a polar phase. P(VDF-TrFE) crystallizes to a much greater extent than PVDF (up to 90% crystalline) yielding a higher remanent polarization, lower coercive field and much sharper hysteresis loops. TrFE also extends the use temperature by about twenty degrees, to close to 100°C. Conversely, copolymers with TFE have been shown to exhibit a lower degree of crystallinity and a suppressed melting temperature as compared to the PVDF homopolymer. Although the piezoelectric constants for the copolymers are not as large as the homopolymer, the advantages of P(VDF-TrFE) associated with processability, enhanced crystallinity, and higher use temperature make it favorable for applications. Typical values of the piezoelectric constants for copolymers with TrFE are given in Table 3.

Recently researchers have reported that highly ordered, lamellar crystals of P(VDF-TrFE) can be made by annealing the material at temperatures between the Curie temperature and the melting point. They refer to this material as a “single crystalline film”. A relatively large single crystal P(VDF-TrFE) 75/25 mol% copolymer has been grown that exhibits a room temperature $d_{33} = -38$ pm/V and a coupling factor $k_{33} = 0.33$ (17).

Zhang et al. (18) have studied the influence of introducing defects into the crystalline structure of P(VDF-TrFE) copolymer using high electron irradiation on electroactive actuation. Extensive structural investigations indicate that the electron irradiation disrupts the coherence of polarization domains (all trans chains) and forms localized polar regions (nanometer-sized, all-trans chains interrupted by trans and gauche bonds). After irradiation, the material exhibits behavior analogous to that of relaxor ferroelectric systems in inorganic materials. The resulting material is no longer piezoelectric but rather exhibits a large electric field-induced strain (5% strain) due to electrostriction. The basis for such large electrostriction is the large change in the lattice strain as the polymer

traverses the ferroelectric to paraelectric phase transition and the expansion and contraction of the polar regions. Piezoelectricity can be measured in these and other electrostrictives when a DC bias field is applied. Irradiation is typically accomplished in a nitrogen atmosphere at elevated temperatures with irradiation dosages up to 120Mrad.

2.1.5. Other semicrystalline polymers.

2.1.5.1. Polyamides. A low level of piezoelectricity was first reported in polyamides (also known as nylons) by Kawai et al. in 1970 (19). A systematic study of odd-numbered nylons, however, initiated by the group of Scheinbeim and Newman in 1980 (20), served as the impetus for more than twenty years of subsequent investigations of the piezoelectric and ferroelectric activity in these polymers. The monomer unit of odd nylons consists of even numbers of methylene groups and one amide group with a dipole moment of $3.7D$. Polyamides crystallize in all-trans conformations and are packed so as to maximize hydrogen bonding between adjacent amine and carbonyl groups as seen in Figure 4 for an even and an odd numbered polyamide. The amide dipoles align synergistically for the odd-numbered monomer, resulting in a net dipole moment. The amide dipole cancels for an even-numbered nylon, although remanent polarizations have been measured for some even-numbered nylons as discussed later in this chapter. The unit dipole density is dependant on the number of methylene groups present and the polarization increases with decreasing number of methylene groups from 58 mC/m^2 for nylon-11 to 125 mC/m^2 for Nylon-5 (8).

Polyamides are known to be hydrophilic. Since the water absorption is associated with hydrogen bonding to the polar amide groups, the hydrophilicity increases as the density of amide groups increases. Water absorption in nylon-11 and nylon-7 has been shown to be as high as 4.5% (by weight), and more than 12% for nylon-5 (21) while it is less than 0.02% for PVDF and its copolymers. Studies have shown that water absorption can have a dramatic effect on the dielectric and piezoelectric properties of nylons, however, the water does not affect the crystallinity or orientation in thermally annealed films (21). Thus, films can be dried to restore their original suite of properties.

At room temperature, odd-numbered nylons have lower piezoelectric constants than PVDF, however, when examined above their glass transition temperature, they exhibit comparable ferroelectric and piezoelectric properties and much higher thermal stability. The piezoelectric d and e constants increase rapidly with temperature. Maximum stable d_{31} values of 17 pC/N and 14 pC/N are reported for Nylon-7 and Nylon-11 respectively. Corresponding values of the electromechanical coupling, k_{31} are 0.054 and 0.049. Studies have also shown that annealing of nylon films enhances their polarization stability as it promotes more dense packing of the hydrogen bonded sheet structure in the crystalline regions and hinders the dipole switching due to lowered free volume for rotation (22).

Though widely studied, piezoelectric polyamides have not been widely employed in applications. This is due in part to its low room temperature piezoelectric response and its problem with moisture uptake.

2.1.5.2. Liquid-crystalline polymers. Liquid crystals consist of highly order rodlike or disklike molecules. At their melting point they partially lose crystalline order, generating a fluid but ordered state. They can form layered structures called smectic phases or nematic phases with an approximately parallel orientation of the molecular long axis. Meyer (23) was the first to predict that spontaneous polarization could be achieved in liquid crystals based on symmetry arguments. Subsequently, it has been shown that liquid crystalline molecules having

chiral carbon atoms linking a mesogenic group and end alkyl chains have the possibility of exhibiting ferroelectric behavior in the smectic C phase (SmC*) (24). In this phase the molecular axis tilts from the normal to the layer plane and the molecular dipoles align in the same direction, yielding a net polarization. If such liquid crystalline molecules are introduced into the backbone or as a side group on a polymer, a ferroelectric liquid crystalline polymer can be obtained. There are three requirements for the appearance of spontaneous polarization in a liquid crystal: a center of chirality; a dipole moment positioned at the chiral center and acting transverse to the molecular long axis; and the existence of a tilted smectic phase (25).

2.1.5.3. Polyureas. Polyureas are thermosets, long used as insulators in a number of applications. Until a few years ago, ureas were available mostly as insoluble powders or highly cross-linked resins. In 1987, Takahashi et al. (26) successfully developed a vapor deposition polymerization method and later applied it to the synthesis of polyureas (27). Typically, a vapor deposition technique is used by evaporating $\text{OCN-R}_1\text{-NH}_2$ and $\text{H}_2\text{N-R}_2\text{-NH}_2$ monomers simultaneously on a substrate (where R_1 and R_2 are various aliphatic or aromatic groups). This prevents cross-linking and allows the processing of thicknesses in the hundreds of nanometers to tens of micrometers.

Takahashi et al. (27) explored the dielectric and pyroelectric properties of polyureas films which led to the discovery of their piezoelectricity. By the early 1990's to the present, various aromatic and aliphatic polyureas were synthesized and shown to be piezoelectric (28, 29). Aromatic polyureas were the first polyurea structures shown to be piezoelectric. They exhibit high temperature stability, and have a piezoelectric e -constant of 15 mC/m^2 , which remains independent of temperature up to 200°C . Their pyroelectric coefficient is high due to their low dielectric loss compared to other polymers. The d -constant is about 5 pC/N at room temperature and increases as temperature increases (28).

Owing to their structures, aliphatic polyureas possess a higher flexibility of their molecular chains. Similarly to polyamides, hydrogen bonds play a large role in stabilizing the orientation polarization that is imparted. Polyureas with odd-numbered methyl groups exhibit an overall non-zero polarization. Polyurea-9 was first synthesized and processed and an e -constant of 5 mC/m^2 was reported (28). Polyureas with a smaller number of carbons were then attempted, since it was surmised that it should lead to a higher density of urea bond dipole. Towards that end, polyurea-5 was synthesized and the e - and d -constants were twice the values of the polyurea-9. Aliphatic polyureas exhibit a ferroelectric hysteresis in addition to being piezoelectric when possessing odd numbers of methyl groups. Their thermal stability and piezoelectric coefficients are highly dependent on the poling temperature (typically 70° to 150°C), but lower than those of aromatic polyureas.

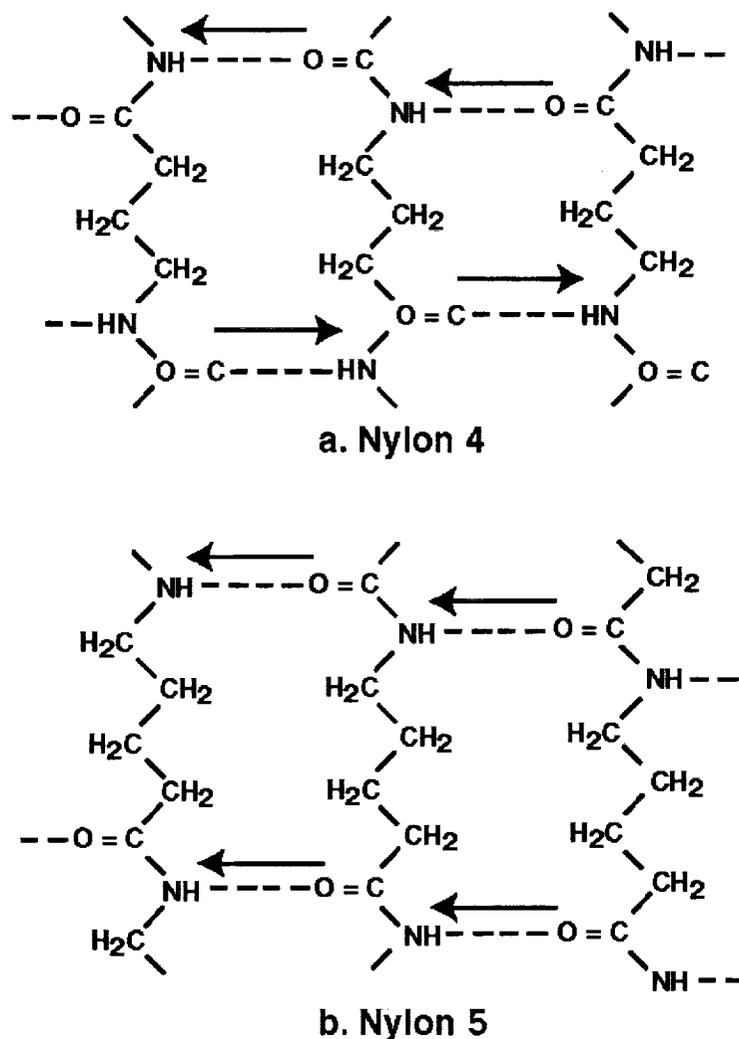


FIG. 4. Schematic depiction of hydrogen-bonded sheets showing dipole directions in the crystal lattices of (a) even (Nylon 4) and (b) odd polyamides (Nylon 5)

2.1.5.4. Biopolymers. Piezoelectricity of biopolymers was first reported for keratin in 1941 (30). When a bundle of hair was immersed in liquid air, an electric voltage of a few volts was generated between the tip and the root. When pressure was applied on the cross section of the bundle, an electric voltage was generated. Subsequently piezoelectricity has been observed in a wide range of other biopolymers including collagen (31, 32), polypeptides like poly- γ -methylglutamate and poly- γ -benzyl-L-glutamate (33, 34), oriented films of DNA (35), poly-lactic acid (36), and chitin (37). Since most natural biopolymers possess D_{∞} symmetry, they exhibit shear piezoelectricity. A shear stress in the plane of polarization produces electric displacement perpendicular to the plane of the applied stress, resulting in a $-d_{14} = d_{25}$ piezoelectric constant. The piezoelectric constants of biopolymers are small relative to synthetic polymers, ranging in value from 0.01 pC/N for DNA to 2.5 pC/N for collagen. The electromechanical effect in such polymers is attributed to the internal rotation of polar atomic groups linked to

asymmetric carbon atoms. Keratin and some polypeptide molecules assume an α -helical or a β crystalline structure in which the CONH dipoles align synergistically in the axial direction.

Currently, the physiological significance of piezoelectricity in many biopolymers is not well understood, but it is believed that such electromechanical phenomena may have a distinct role in biochemical processes. For example, it is known that electric polarization in bone influences bone growth (38). In one study a piezoelectric PVDF film was wrapped around the femur of a monkey. Within weeks, a remarkable formation of new bone was observed. The motion of the animal caused deformation of the film producing a neutralizing ionic current in the surrounding tissue. This minute fluctuating current appears to stimulate the metabolic activity of bone cells and to lead to proliferation of bone.

2.2. Amorphous Polymers. The purpose of the following section is to explain the mechanism and key components required for developing piezoelectricity in amorphous polymers and to present a summary of polarization and electromechanical properties of amorphous polymers currently under investigation.

2.2.1. Mechanism of piezoelectricity.

2.2.1.1. Dielectric theory. The piezoelectricity in amorphous polymers differs from that in semi-crystalline polymers and inorganic crystals in that the polarization is not in a state of thermal equilibrium, but rather a quasi-stable state due to the freezing-in of molecular dipoles. The result is a piezoelectric-like effect. A theoretical model for polymers with frozen-in dipolar orientation was presented to explain piezoelectricity and pyroelectricity in amorphous polymers such as polyvinyl chloride (39).

One of the most important properties of an amorphous piezoelectric polymer is its glass transition temperature (temperature below which the material exhibits glass-like characteristics, and above which it has rubber-like properties) as it dictates use temperature and defines the poling process conditions. Orientation polarization of molecular dipoles is responsible for piezoelectricity in amorphous polymers. It is induced, as shown in Figure 5, by applying an electric field, E_p at an elevated temperature ($T_p \geq T_g$) where the molecular chains are sufficiently mobile and allow dipole alignment with the electric field. Partial retention of this orientation is achieved by lowering the temperature below T_g in the presence of E_p , resulting in a piezoelectric-like effect. The remanent polarization, P_r is directly proportional to E_p and the piezoelectric response. The procedure used to prepare a piezoelectric amorphous polymer clearly results in both oriented dipoles and space or real charge injection. The real charges are usually concentrated near the surface of the polymer, and they are introduced due to the presence of the electrodes. Interestingly, some researchers (40, 41) have shown that the presence of space charges does not have a significant effect on the piezoelectric behavior. The reason is two fold. The magnitude of the space charges is usually not significant with respect to the polarization charges. Secondly, space charges are essentially symmetrical with respect to the thickness of the polymer, therefore, when the material is strained uniformly the contribution to the piezoelectric effect is negligible.

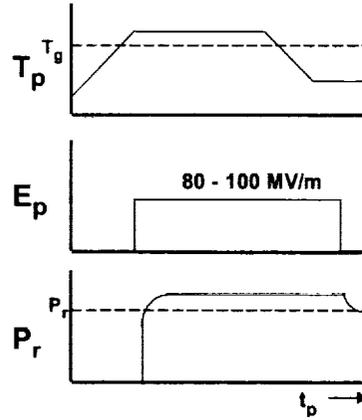


FIG. 5. Poling profile for an amorphous polymer.

In what follows, the origins of the dielectric contribution to the piezoelectric response of amorphous polymers is addressed. The potential energy U of a dipole μ at an angle θ with the applied electric field is $U = \mu E \cos \theta$. Using statistical mechanics and assuming a Boltzmann's distribution of the dipole energies, the mean projection of the dipole moment, $\langle \mu \rangle_E$, in the direction of the applied electric field is obtained

$$\frac{\langle \mu_E \rangle}{\mu} = \coth \frac{\mu E_p}{kT} - \frac{kT}{\mu E} \quad (8)$$

This is the Langevin equation which describes the degree of polarization in a sample when an electric field, E , is applied at temperature T . Experimentally, a poling temperature in the vicinity of T_g is used to maximize dipole motion. The maximum electric field which may be applied, typically 100 MV/m, is determined by the dielectric breakdown strength of the polymer. For amorphous polymers, $\mu E / kT$ is much less than one, which places these systems well within the linear region of the Langevin function. The remanent polarization P_r is simply the polarization during poling minus the electronic and atomic polarizations that relax at room temperature once the field E_p is removed. The following linear equation for the remanent polarization results when the Clausius Mossotti equation is used to relate the dielectric constant to the dipole moment (42)

$$P_r = \Delta \epsilon \epsilon_0 E_p \quad (9)$$

It can be concluded that remanent polarization and hence piezoelectric response of a material is determined by $\Delta \epsilon$, making it a practical criterion to use when designing piezoelectric amorphous polymers. The dielectric relaxation strength, $\Delta \epsilon$ may be the result of either free or cooperative dipole motion. Dielectric theory yields a mathematical approach for examining the dielectric relaxation due to free rotation of the dipoles, $\Delta \epsilon$. The equation incorporates Debye's work based on statistical mechanics, the Clausius Mossotti equation, and the Onsager local field, and neglects short range interactions (43)

$$\Delta\varepsilon_{\text{calculated}} = \frac{N\mu^2}{3kT\varepsilon_0} \left(\frac{n^2+2}{3}\right)^2 \left(\frac{3\varepsilon(0)}{2\varepsilon(0)+n^2}\right)^2 \quad (10)$$

N is the number of dipoles per unit volume, k is the Boltzmann constant, $\varepsilon(0)$ is the static dielectric constant and n is the refractive index. One way to measure P_r for amorphous polymers requires the thermally stimulated current (TSC) method (refer to section on characterization). P_r can be calculated from the liberated charge during TSC, and by reconciling that with the Onsager relation, the dipole density can be calculated:

$$P_r = \frac{N\mu^2 E_p}{3kT_p} \left(\frac{\varepsilon_\infty+2}{3}\right)^2 \left(\frac{3\varepsilon(0)}{2\varepsilon(0)+\varepsilon_\infty}\right) \quad (11)$$

The piezoelectric constants are related to the polarization. From basic thermodynamics, we have:

$$d_{3i} = \left(\frac{\partial P}{\partial \sigma_i}\right)_{\gamma, T} \quad (12)$$

Mopsik and Broadhurst (41) have developed a molecular theory of the direct piezoelectric effect in poled amorphous piezoelectric polymers. In their paper, they found the expression for the hydrostatic coefficient. Later, this theory was extended and an equation for d_{3i} was obtained (44, 45). By differentiating equation (11) above and modifying it to account for dimensional effects such as in the case of stretching (44, 46)

$$d_{3i} = P_r(1-\gamma)S_{11} + \frac{P_r(1-\gamma)}{3}(\varepsilon_\infty-1)S_{11} \quad (13)$$

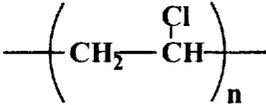
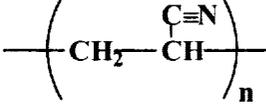
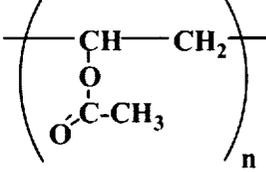
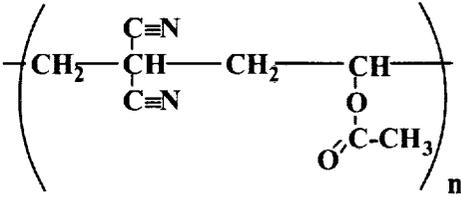
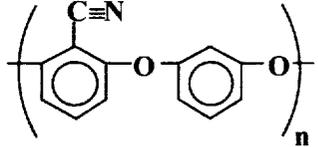
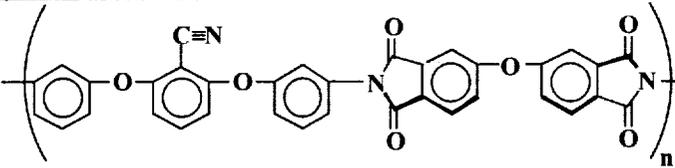
where γ is the Poisson's ratio, ε_∞ is the permittivity at high frequencies, and S_{11} is the compliance of the polymer. The first term accounts for dimensional effects and the second term gives the contribution of the local field effect.

2.2.1.2. Polarizability and poling conditions. Designing an amorphous polymer with a large dielectric relaxation strength and hence piezoelectric response requires the ability to incorporate highly polar groups at high concentrations and cooperative dipole motion. A study of the relationship between relaxation times, poling temperatures and poling fields is crucial to achieve optimal dipole alignment. Theoretically, the higher the electric field, the better the dipole alignment. The value of the electric field is limited, however, by the dielectric breakdown of the polymeric material. In practice, 100 MV/m is the maximum field that can be applied to these materials. Poling times need to be of the order of the relaxation time of the polymer at the poling temperature.

During poling, the temperature is lowered to room temperature while the field is still on, in order to freeze in the dipole alignment. In a semicrystalline material, however, the locking-in of the polarization is supported by the crystalline structure of the polymer, and is therefore stable above the glass transition temperature of the polymer. Since the remanent polarization in amorphous polymers is lost in the vicinity of T_g , their use is limited to temperatures well below T_g . This means that the polymers are used in their glassy state, when they are quite stiff thus limiting the ability of the polymer to strain with an applied stress. The piezoelectric amorphous polymer may be used at temperatures near its T_g to optimize the mechanical properties, but not too close so as to maintain the remanent polarization.

Although there is little data addressing the stability of piezoelectric activity in amorphous polymers, it is clear that time, pressure, and temperature can all contribute to dipole relaxation in these polymers. For a given application and use temperature, the effect of these parameters on the stability of the frozen-in dipole alignment should be determined.

TABLE 4.
Structure, polarization and T_g for piezoelectric amorphous polymers.

Polymer	Structure	T_g (°C)	d_{31} (pC/N)	P_r (mCm ²)	Reference
PVC		80	5	16	44
PAN		90	2	25	49
PVAc		30	-	5	59
P(VDCN-VAc)		170	10	50	51
PPEN		145	-	12	55
(β-CN) APB/ ODPA		220	5@ 150 °C	20	59

2.2.2. Examples of amorphous piezoelectric polymers. The literature on amorphous piezoelectric polymers is much more limited than that for semicrystalline systems. This is in part because no amorphous piezoelectric polymers have exhibited responses high enough to attract commercial interest. Much of the previous

work on amorphous piezoelectric polymers resides in the area of nitrile substituted polymers including polyacrylonitrile (PAN) (47-49), poly(vinylidene cyanide vinylacetate) (PVDCN/VAc) (50-54), polyphenylether-nitrile (PPEN) (55, 56) and poly(1-bicyclobutanecarbonitrile) (57). Weak piezoelectric activity in polyvinyl chloride (PVC) and polyvinyl acetate (PVAc) has also been found (11, 41, 58, 59). The most promising of these materials are the vinylidene cyanide copolymers that exhibit large dielectric relaxation strengths and strong piezoelectricity. Table 4 shows molecular structures of the most commonly encountered amorphous piezoelectric polymers.

2.2.2.1. Polyvinylidene chloride (PVC). The carbon-chlorine dipole in polyvinylidene chloride (PVC) has been oriented to produce a low level of piezoelectricity. The piezoelectric and pyroelectric activities generated in PVC were found to be stable and reproducible. Broadhurst et al. (39) used PVC as a basis for understanding and studying piezoelectricity in amorphous polymers. The piezoelectric coefficients d_{31} of PVC has been reported in the range of 0.5 to 1.3 pC/N. An improved response was achieved by simultaneous stretching and corona poling of film (44). The enhanced piezoelectric coefficient d_{31} ranged from 1.5 to 5.0 pC/N.

2.2.2.2. PVDCN-copolymers. In 1980, exceptionally strong piezoelectric activities were found by Miyata et al. (50) for the amorphous copolymer of VDCN and VAc. The copolymer was poled at 150°C (20°C below its T_g) and cooled to room temperature under the electric field. A $P_r = 55$ mC/m² was obtained for a poling field of 50 MV/m. That is comparable to the P_r of PVDF. When local ordering, or paracrystallinity, is inherent in the polymer or is induced by mechanical stretching, an increase in the value of the remanent polarization is observed. For example, some researchers (51) assert that the large discrepancy between the measured and calculated $\Delta\epsilon$ for PVDCN-VAc may be attributed to locally ordered regions in the polymer. For the copolymer PVDCN/VAc, $\Delta\epsilon_{calculated} = 30$ while $\Delta\epsilon_{measured} = 125$ (51). This large discrepancy in the values of $\Delta\epsilon$ is indicative of cooperative motion of several nitrile dipoles within the locally ordered regions of the polymer. Cooperativity means that instead of each dipole acting independently, multiple nitrile dipoles respond to the applied electric field in a unified manner. Although the existence of cooperative dipole motion clearly increases the piezoelectric response of amorphous polymers, the mechanisms by which cooperativity can be systematically incorporated into the polymer structure remain unclear at this time (59).

The large relaxation strength exhibited by PVDCN/VAc gives it the largest value of P_r and hence d_{31} of all the amorphous polymers. A number of authors have suggested that PVDCN-VAc also exhibits ferroelectric-like behavior (51-53) due to switching of the nitrile dipoles under an AC-field. The switching time is long compared to normal ferroelectric polymers.

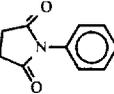
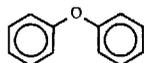
2.2.2.3. Other VDCN polymers. The homopolymer of vinylidene cyanide is thermally unstable (60) as well as highly sensitive to moisture, but VDCN can be polymerized with a variety of monomers in addition to VAc, such as vinyl benzoate (VBz), methyl methacrylate (MMA) and others forming highly alternating chains. All of these copolymers show some degree of piezoelectricity although lower than PVDCN-VAc, which is explained by different activation energies for dipole orientation in the glassy state and different chain mobility depending on the side group.

2.2.2.4. Polyacrylonitrile (PAN). Polyacrylonitrile (PAN) is one of the most widely used polymers. Shortly after the PVDCN-VAc system was shown to be piezoelectric, researchers turned their attention to PAN, due to its similarity with the aforementioned polymers. The presence of the large nitrile dipole in PAN indicated that it can be oriented by an applied electric field. PAN presented some challenges not encountered in other nitrile-substituted polymers however. Although theoretical calculations predicted a strong piezoelectric behavior, it was difficult to pole. Several investigators (47-49) have proposed that the difficulty of poling PAN in the unstretched state is related to the strong dipole-dipole interaction of nitrile groups of the same molecule which repel each other, thus preventing normal polarization. Upon stretching, the intermolecular dipole interactions facilitate the packing of the individual chains and give rise to ordered zones. Comstock et al. (47) measured the remanent polarization of both unstretched and stretched PAN using the thermally stimulated current method (TSC) and observed a two-fold increase in the remanent polarization (TSC peak at 90°C) for PAN that was stretched four times its original length. Another approach is the copolymerization of PAN with another monomer. Researchers have successfully reported a reduction of the hindering effect of the dipole-dipole interactions and an enhancement of the internal mobility of the polymer segments when PAN is copolymerized with polystyrene or methylmethacrylate. Berlepsch et al. (49) observed a ferroelectric behavior in P(AN-MMA), where, for given temperature and field conditions, a characteristic hysteresis loop is obtained. They concluded that it was perhaps one rare example where both ferroelectric and frozen-in dipole orientations were superimposed.

2.2.2.5. Nitrile-substituted polyimide. Amorphous polyimides containing polar functional groups have been synthesized (61-63) and investigated for potential use as high temperature piezoelectric sensors. (β -CN) APB/ODPA, polyimide is one such system. The (β -CN) APB/ODPA polyimide possesses the three dipole functionalities shown in Table 5. Typically, the functional groups in amorphous polymers are pendant to the main chain. The dipoles, however, may also reside within the main chain of the polymer, such as the anhydride units in the (β -CN) APB/ODPA polyimide. The nitrile dipole is pendant to a phenyl ring ($\mu=4.2$ D), while the two anhydride dipoles ($\mu= 2.34$ D) are within the chain, resulting in a total dipole moment per repeat unit of 8.8 D.

TABLE 5.

Values of the dipole moments within the nitrile-substituted polyimide

Dipoles	Dipole identity	Dipole Moment (Debye)
	Pendant nitrile group	4.18
	Main chain dianhydride group	2.34
	Main chain diphenylether group	1.30

The remanent polarization P_r of the (β -CN)APB/ODPA system by the thermally stimulated current method (TSC) was approximately 20mC/m^2 when poled at 80MV/m for one hour above T_g (64). Excellent thermal stability was observed up to 100°C , and no loss of the piezoelectric response was seen after aging at 50°C and 100°C up to 500 hrs.

In an attempt to enhance dipolar orientation and minimize localized arcing during poling, partially-cured films of the (β -CN)APB/ODPA system were simultaneously corona poled and cured. The aligned polar groups should be immobilized by additional imidization and subsequent cooling in the presence of an electric field. Park et al. (64) found that both the T_g and the degree of imidization increased almost linearly with the final cure temperature. The value of P_r appeared to be higher for films cured at lower temperatures. The mobility of the molecules in a partially imidized state should be higher than that of the fully cured one, therefore producing a higher degree of dipole orientation.

The importance of dipole concentration on ultimate polarization is evident from a comparison of polyacrylonitrile (PAN) and the polyimide (β -CN) APB/ODPA. PAN has a single nitrile dipole per repeat unit ($\mu=3.5D$) resulting in a dipole concentration of $1.34 \times 10^{28} \text{ m}^{-3}$. This translates into an ultimate polarization of 152 mC/m^2 (20). The (β -CN) APB/ODPA polyimide, on the other hand, has a total dipole moment per monomer of $8.8 D$. The dipole concentration of (β -CN) APB/ODPA, however, is only $0.136 \times 10^{28} \text{ m}^{-3}$, resulting in an ultimate polarization of 40 mC/m^2 , which is less than a fourth of that of PAN. As a result, similar polyimides with increased nitrile concentrations were synthesized and characterized. Studies on these polymers show polarization is significantly increased by increasing dipole concentration. Structure-property investigations designed to assess effects of these dipoles on T_g , thermal stability, and overall polarization behavior are currently being pursued.

2.2.2.6. Even numbered nylons. Murata et al. (65) have shown that Nylon 6I and 6I/6T exhibits a D-E hysteresis loop over a temperature range of 30 to 65°C at a fixed maximum field of 168 MV/m . The remanent polarization increased with increasing temperature. It should be noted that Nylon 6I and 6I/6T were shown to be completely amorphous. The P_r was about 30 mC/m^2 .

2.2.2.7. Aliphatic polyurethane. Some researchers (1) have suggested that aliphatic polyurethane systems exhibit ferroelectricity that stems from the amorphous part at temperatures above the glass transition temperature. This "liquid state" ferroelectricity is very peculiar, seems to exist, and is supported by the hydrogen bonds present.

3. Characterization and Modeling.

3.1. Characterization. Most piezoelectric characterization methods were developed for crystalline ceramics, and had to be adapted for piezoelectric polymers. Methods based on resonance analysis and equivalent circuits can be used to characterize semi-crystalline PVDF and its copolymers, as outlined by IEEE standards (66). Details on applying the resonance analysis to piezoelectric polymers have recently been explored by Sherrit and Bar-Cohen (67). Due to the lossy nature of some polymers, the IEEE standards are not adequate, and other techniques are needed to describe the piezoelectric properties more accurately.

Quasi-static direct methods are both versatile and well suited to fully investigate the piezoelectric response of polymers. Direct methods of this type are especially appropriate for amorphous polymers. Thermally stimulated current measurements (TSC) (68) are used to measure the remanent polarization imparted to a polymer, and direct strain or charge measurements are used to investigate the piezoelectric coefficients with respect to electric field, frequency, and stress.

TSC is a valuable tool for characterizing piezoelectric polymers. After poling the polymer, a measure of the current dissipation and the remanent polarization as a function temperature can be obtained through the TSC. As the sample is heated through its glass transition temperature (or Curie temperature in the case of a semicrystalline polymer) at a slow rate (typically 1-4°C/min), the depolarization current is measured using an electrometer. The remanent polarization is equal to the charge per unit area; and is obtained from the data by integrating the current with respect to time and plotting it as a function of temperature:

$$P_r = \frac{Q}{A} = \frac{1}{A} \int i(t) dt \quad (14)$$

Figure 6 illustrates a typical TSC result. Since permanent dipoles are essentially immobile at temperatures well below T_g , the current discharge remains low in this temperature range. As temperature increases to and beyond the T_g , however, the onset of dipole mobility contributes to a significant increase in the current peak. The peak in the current and the subsequent polarization maximum usually occurs in the vicinity of the T_g .

Direct methods for measuring the strain that results from application of a field, (or vice versa), applying a strain, and measuring the accumulated charge, are abundant. To evaluate the piezoelectric strain (converse effect), interferometers, dilatometers, fiber optic sensors, optical levers, linear variable displacement transducers and optical methods are employed (69-72). The “out-of-plane” or thickness piezoelectric coefficient, d_{33} , can be ascertained as a function of driving field and frequency. The coefficient is measured based on the equation:

$$S_{33} = d_{33} E_3 \quad (15)$$

where S_{33} is the strain and E_3 is the applied electric field.

A modified Rheovibron, or similar techniques, have been used to measure the direct piezoelectric effect, where charges accumulated on the surfaces of the polymer are measured (59). The piezoelectric coefficient, d_{31} , can be obtained by straining the polymer along the direction of applied stress with a force F . A charge Q is generated on the surface of the electrodes. A geometric factor is used to produce a geometry independent parameter, i.e., surface charge density per unit applied stress,

$$d_{31} = \frac{Q/(WL)}{F/(Wt)} \quad (16)$$

which has units of pC/N. W , L and t are the width, length, and thickness of the sample respectively.

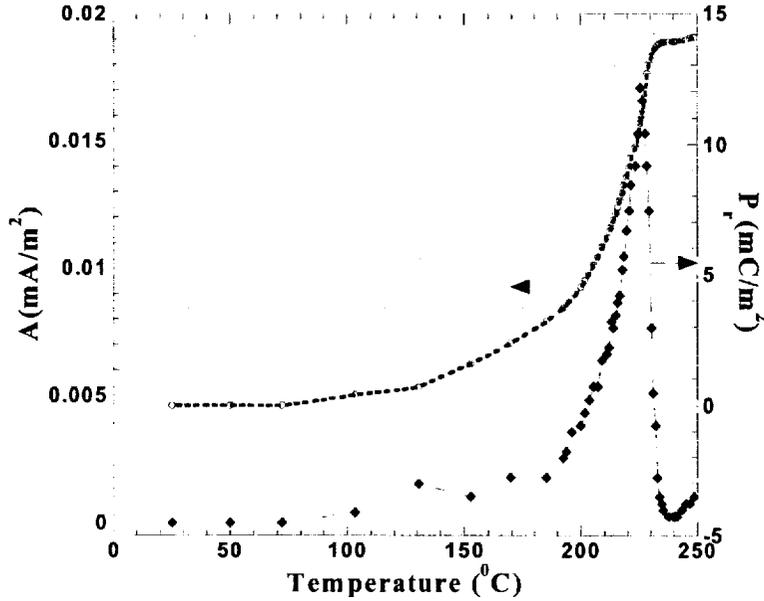


FIG. 6. Thermally stimulated current plot for typical amorphous poled polymer.

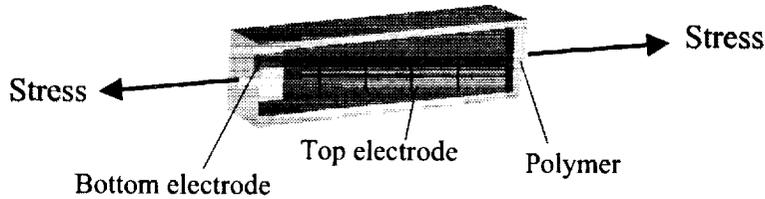


FIG. 7. Direct effect in polymers

3.2. Modeling. The methodology for modeling piezoelectric behavior in polymers varies depending on the targeted properties. Approaches cover the range from macroscale to micro and atomistic scales. A detailed review of computational methods applied to electroactive polymers has been published (73).

In some cases, modeling can predict behavior where experiments cannot. Using molecular dynamics, the orientation polarization of the (β -CN) APB/ODPA polymer has been assessed by monitoring the angle, θ , that the dipoles make with an applied electric field (74). The bulk P_r was calculated and the results agreed extremely well with experimental results (61). Computational modeling, however, gave insight into the contributions of the various dipoles present in a way experimental results could not. The model predicted that 40% of the orientation polarization was due to the dianhydride within the backbone of the ODPA monomer, and demonstrated the importance of the flexible ether linkage (oxygen atom) in facilitating dipole alignment. Modeling insight of this kind is invaluable in guiding the synthesis of new materials.

Modeling of PVDCN-VAc can also play a role in understanding the cooperative motion responsible for the high dielectric relaxation strength of this class of polymers; a fact not possible experimentally (75). Recently, meso-scale simulation was used to describe polarization reversal in PVDF films (76).

4. Applications and Future Considerations. The application potential for piezoelectric and other electroactive polymers is immense. To date, ferroelectric polymers have been incorporated into numerous sensing and actuation devices for a wide array of applications. Typical applications include devices in medical instrumentation, robotics, optics, computers, and ultrasonic, underwater and electroacoustic transducers. One important emerging application area for electroactive polymers is in the biomedical field where polymers are being explored as potential artificial muscle actuators, as invasive medical robots for diagnostics and microsurgery, as actuator implants to stimulate tissue and bone growth, and as sensors to monitor vascular grafts and to prevent blockages (77, 78). Such applications are ideal for polymers since they can be made to be biocompatible and they have excellent conformability and impedance matching to body fluids and human tissue. The intent of this chapter is not to detail specific applications but the interested reader may refer to excellent sources on applications of piezoelectric and ferroelectric polymers (79-81).

In the future, we believe that fertile research areas for piezoelectric polymers will include work to enhance their properties; to improve their processability for incorporation into devices, and to develop materials with a broader use temperature range. Fundamental structure-property understanding has enabled the development of numerous semicrystalline and amorphous polymers. Based on this knowledge base, future research which focuses on property enhancement via new chemistries with higher dipole concentrations and incorporation of dipole cooperativity may yield improved materials. Property enhancements may also be gained from processing studies to alter polymer morphology such as those used to make "single crystalline" fluoropolymers. Development of materials that can operate in extreme environments (high temperature and subambient temperature) is also important for expanding the utilization of piezoelectric polymers. Piezoelectric and pyroelectric constants of polymers are considerably lower than for ferroelectric inorganic ceramics. Improvements in properties by incorporating polymers into composites with inorganics to obtain higher electromechanical properties and better mechanical properties is also valuable. To date piezoelectric polymer-ceramic composites have been made wherein the polymer serves only as an inactive matrix for the active ceramic phase. This is due to the mismatch in permittivity between the polymer and ceramic which makes it difficult to pole both phases. Research resulting in active polymer and ceramic phases could yield interesting electromechanical properties.

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13. ABSTRACT (Maximum 200 words) The purpose of this review is to detail the current theoretical understanding of the origin of piezoelectric and ferroelectric phenomena in polymers; to present the state-of-the-art in piezoelectric polymers and emerging material systems that exhibit promising properties; and to discuss key characterization methods, fundamental modeling approaches, and applications of piezoelectric polymers. Piezoelectric polymers have been known to exist for more than forty years, but in recent years they have gained notoriety as a valuable class of smart materials.				
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