Chapter 23

Piezoelectric Polymers
and their Applications

23.1. Introduction

The piezoelectric effect on a polymer was revealed for the first time in Poly(vinylidene fluoride (PVDF) by Heiji Kawaï, in 1969 [KAW 69]. In general, piezoelectricity corresponds to the outbreak, or the variation, of a polarization in a material in response to the application of a mechanical stress: a phenomenon designated as the direct effect. This type of material also produces the opposite effect: the application of an electric field causes a deformation of the sample. These electrical and mechanical properties when coupled with polymers are used in several applications, such as receiving and transmitting transducers.

PVDF and its copolymer vinylidene fluoride (VDF) with trifluoroethylene (TrFE) or tetrafluoroethylene (TFE) groups are materials whose ferroelectricity has been demonstrated [LOV 83, FUR 89], and which is developed in section 23.3.1. In these semi-crystalline polymers, it is the spontaneous polarization of the crystalline phase which causes their piezoelectricity. Fluorinated polymers have good piezoelectric properties associated with intrinsic properties of softness, lightness, etc. These organic materials thus have an interesting place in applications such as transducers, for example, in comparison with a piezoelectric ceramic, the lead zirconate titanate (PZT) which is also widely used.

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More recently, ferroelectric properties have been shown in other semi-crystalline polymers: the odd-numbered polyamides [MEI 93]. These polyamides possess interesting piezoelectric properties, but their sensitivity to hydration has not yet permitted a commercial development [NEW 90].

Research devoted to piezoelectric amorphous polymers are much less numerous, because a piezoelectric activity is often insufficient to be developed in applications. The first studies were undertaken on polymers substituted for nitrile such as polyacrylonitrile (PAN) or vinylidene cyanide and vinyl acetate copolymers (PVDCN/VAc) [MIY 80]. Amongst these materials, the most promising ones are the vinylidene cyanide copolymers, which possess better values of piezoelectric constants and of the dielectric relaxation intensity $\Delta\varepsilon$. The origin of piezoelectricity in amorphous polymers is different to that which is observed in semi-crystalline polymers and inorganic crystals. Indeed, polarization in piezoelectric amorphous polymers does not correspond to a thermodynamic equilibrium state, but rather to a quasi-stable state of fixed molecular dipoles.

Fluorinated polymers can thus be used to make electroacoustic transducers such as loudspeakers, headphones, microphones, probes for medical echography, underwater acoustic hydrophones, acoustic emission probes for non-destructive testing [CHE 95, NAL 95]. These devices are distinguished from usual transducers by their active membrane which generally does not require any acoustic matching layers to the propagation medium. Their performances are also improved, owing to the possibility of giving the membrane a geometry calculated beforehand, by use of thermoforming processes [RAV 81].

In this chapter, we shall develop the properties of piezoelectric polymers in relation to their physical and chemical structure. We shall then present their specificities in several examples of electroacoustic and ultrasonic transducer applications in the biomedical and Non-Destructive Testing (NDT) domains.

## 23.2. Piezoelectric polymeric materials

23.2.1. *Poly(vinylidene fluoride)(PVDF)*

Poly(vinylidene fluoride) is a semi-crystalline thermoplastic polymer with a relatively simple chemical structure $[-CH_2-CF_2-]_n$, where n is typically larger than 10,000. Figure 23.1 shows that the constitutive motif possesses a strong dipole moment $\mu_i = 7.56 \ 10^{-30}$ C.m [MAR 82] due to the presence of two fluoride atoms and the dissymmetry of the molecule. The dipole moment is defined by $\mu_i = q \ .d$, where d is the distance which separates two concentrated charges $+q$ and $-q$.

PVDF crystallizes in the shape of lamellae, called crystallites, whose thickness is generally of the order of a few tens of nanometers. The macromolecules are coiled up within these lamellae with blades perpendicular to both sides. These crystallites are arranged into essentially spherically symmetric polycrystalline aggregates designed as spherolites. The increase in crystallites occurs in a radial manner from nucleation centers which constitute the core of the spherolites. Apart from crystallites, the arrangement of macromolecules is made in a disordered manner. The volume not occupied by the crystallites is therefore amorphous. Globally, the polymer is semi-crystalline (a biphasic structure) and its crystallinity rate is of the order of 50 to 55%.

It seems that the ferroelectric properties strongly depend on the crystalline structure of the material. Indeed, numerous studies [KEP 92, SER 80] reveal that the crystalline structure of PVDF mainly present four polymorph phases. The most commonly observed structure, obtained primarily by quenching from the melt, is the non-polar α-phase. The phase which presents the most interest for electro-active properties is the ferroelectric β-phase. The other two phases are referenced as γ- and δ-phases which are also ferroelectrics. Nevertheless, the contributions of these γ- and δ-phases in the ferroelectric properties are neglected because they are constituted of cells that have one very weak dipole moment in comparison with that of the β-phase.

The α-phase of PVDF is constituted of chains in a tg+tg$^-$ formation, whereas β-phase consists of all-trans chains (ttt) (Figure 23.1). The crystalline group of phase α remains uncertain because of the conformational disorder associated with this phase, which is either orthorhombic or monoclinic, depending on the observations made. The β-phase is orthorhombic.
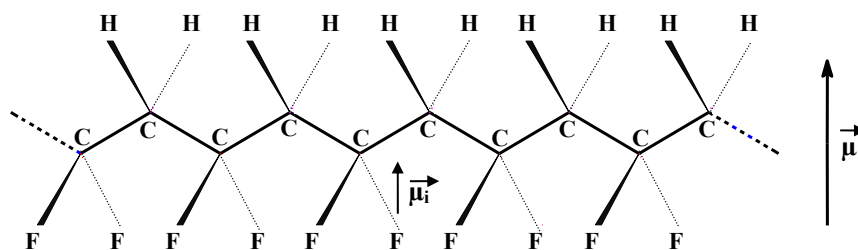

Figure 23.1. *"All-trans" conformation (β-phase) of macromolecular PVDF chains*

Figure 23.1 shows that the dipole moment $\mu = \sum \mu_i$ associated with the macromolecule is at a maximum when the configuration of the chain is in β-phase. Indeed, in this case, the carbonated chain takes all-trans conformation, thus all the CF2 dipoles are oriented in the same direction and the dipoles are added. Thus, the dipole moments oriented in a preferred direction create a macroscopic polarization P effective for each crystallite: this phenomenon causes the ferroelectric properties of the β-phase in PVDF. On the other hand, the α-phase of PVDF is apolar, although the dipole moment of the chain is not null. These dipole moments cancel each other out within a crystalline cell and therefore do not present any electro-active properties. Only PVDF in β-phase will be used as a ferroelectric material for piezoelectric applications.

The calculation of interaction energies of electrostatic and Van Der Waals forces by dissociating the inter- and intra-molecular components shows that the α-phase of PVDF is more stable than the β-phase [SER 80]. PVDF therefore crystallizes naturally in its α-phase.

The crystallization of PVDF is strongly affected by the presence of sequence defects in the macromolecular chain. These defects present themselves in the form of an inversion of one or several monomers: "head-head" (h-h) or "tail-tail" (t-t) bonds (Figure 23.2).

$$-CH_2-CF_2-CH_2-CF_2-CF_2-CH_2-CH_2-CF_2-CH_2-CF_2-$$
$$\uparrow \qquad \uparrow$$
$$\text{h-h} \qquad \text{t-t}$$
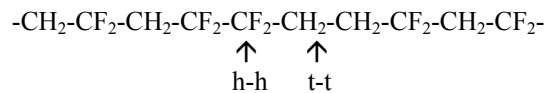
Figure 23.2. *Examples of monomer inversion with a consecutive CF2 – CF2 designed by head-head (h-h) bond and a consecutive CH2 – CH2 for a tail-tail (t-t) bond*

Generally, the rate of sequence defects is of the order of 3 to 6%. The increase in this rate allows a gradual passage of α-phase towards β-phase. A rate greater than 15.5% permits a crystallization to be obtained in the β-phase.

The crystallization in the β-phase is usually obtained by a mechanical extension of films at a temperature near to 100°C in the α-phase. This stretching of a film from 3 to 5 times its initial length causes a breakdown of the original spherulitic structure into an array of crystallites whose molecules are oriented in the direction of the force. Figure 23.6 (below) schematizes the film thus oriented, composed of crystallites scattered in an amorphous phase, where these crystallite axes are oriented in a preferred direction.

23.2.2. *The copolymers P(VDF-TrFE)*

Poly(vinylidene fluoride -trifluoroethylene) copolymers are obtained during synthesis by the introduction of a trifluoroethylene group –CF2-CFH- in PVDF chains. A copolymer possessing 25% of trifluoroetylene entities (in molar percentage) is designated by P(VDF-TrFE) 75-25.

In these copolymers, the arrangement of VDF and TrFE monomers is statistical. They behave like PVDF homopolymers in which some hydrogen atoms were replaced by fluoride atoms: they only possess, for example, one fusion temperature and only one glass transition.

The copolymer of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) produces h-h type sequence defects in the PVDF chain, and thus favors an "all-trans" configuration macromolecule [FUR 89, NAL 95]. The P(VDF-TrFE) copolymers therefore crystallize naturally in the ferroelectric β-phase. This natural crystallization in the β-phase is obtained for concentrations in TrFE monomers ranging between 17 and 50%. The electro-active properties of these copolymers are very similar to those of PVDF and have the same origin. Nevertheless, the rate of trifluoroethylene units strongly influences certain physical properties of these copolymers.

The exact crystalline structure depends on the amount of trifluoroethylene entities. Matrix distorsions of the β-phase of PVDF gradually appear with an increase in the number of TrFE monomers, such that the TrFE unit rate must remain less than about 50% to conserve electro-active properties.

### 23.2.3. *The odd-numbered polyamides*

Polyamides are semi-crystalline thermoplastic polymers. In general, the chemical formula of polyamide x is written:

$$[-(CH_2)_{x-1}-CO-NH-]_n \qquad [23.1]$$
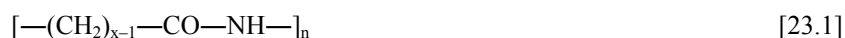
The number x represents the amount of carbon atoms of the repetition unit. The constituent motif is therefore composed of an apolar "paraffin" sequence (sequence of methylenes -CH_2- groups), a variable length which depends on the considered polymer, and a very polar amide group. The value of the dipole moment associated with the amide group is $\mu = 1.18.10^{-29}$ C.m [MEI 93]. We can distinguish even-numbered polyamides possessing an even number of carbon atoms in the repetition unit from odd-numbered polyamides possessing an odd number of carbon atoms.

The molecular cohesion and the physical properties of polyamides are dominated by the electrostatic interactions existing between the amide groups of adjacent chains. These strong interactions lead to the formation of hydrogen bonds between neighboring chains (Figures 24.2.a and 24.2.b). They play a role of first importance in the formation and stability of crystalline zones, and in the cohesion of the amorphous phase.

The arrangement of macromolecular chains in the crystalline zones has been studied in detail for several decades [SCH 92, LOV85]. In crystalline zones of even and odd polyamides, the chains adopt a planar zigzag conformation (the most favorable structure). The existence of hydrogen bonds between adjacent chains leads to the formation of a structure "in sheets" ("*Hydrogen-bonded sheets*").
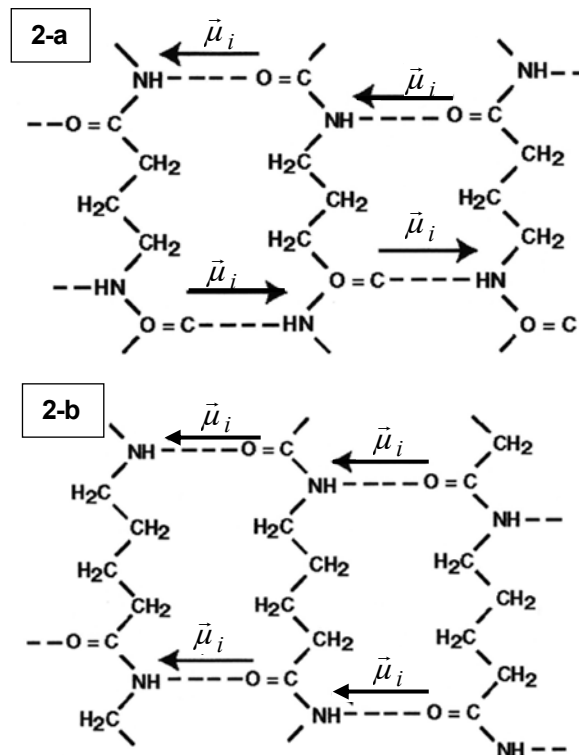
Figure 23.3. *Model of crystalline arrangement of the PA4 (2a) and the PA5 (2b)*

For each type of polyamide, either even and odd, two structures are conceivable: an antiparallel structure and a parallel structure, respectively. An example of these

structures is presented for PA4, Figure 23.3.a, and for the PA5, Figure 23.3.b. For odd polyamides, the parallel structure is the most favorable. On the other hand, for even polyamides, the antiparallel structure is the most favorable because it leads to the formation of a maximal rate of formed hydrogen bonds. In the case of odd polyamides, all the dipoles are aligned in the same direction, whereas for even polyamides, they are inversed two by two. This molecular arrangement causes the ferroelectric properties of odd polyamides: the dipole moments oriented in a preferred direction creates an effective macroscopic polarization P for each crystallite.

The ferroelectric properties of odd polyamides depend on the implementation conditions of the films. The optimal properties were obtained for films quenched from the melted state and stretched in a uniaxial manner (three times the initial length), then annealed at high temperature [MAT 84]. These films present a "double-orientation": the polymeric chains are preferentially oriented in the direction of the stretching, and the sheets made up of the hydrogen bonds are oriented parallel to the film plane.

Polyamides possess an important hydrophilic character. The maximal amount of water which can be absorbed increases as a function of the density of amide groups, i.e. when the paraffin sequence size of the polymer decreases. Thus, the amount of water absorbed in bulk can reach 4.5% in PA11 and PA7, and 12% in PA5, while it is less than 0.02% in PVDF. The physical properties of polyamides are affected by the amount of absorbed water: variation in the mechanical modulus and the dielectric permittivity. Only the amorphous phase is directly affected by the hydration rate, since the water molecules are not diffused in the crystalline phase.

23.2.4. *Copolymers constituted of vinylidene cyanide monomer*

Vinylidene cyanide (VDCN) is an extremely reactive monomer which polymerizes readily with a wide variety of common monomers, such as vinyl acetate or styrene. Most of these copolymers have a high melting or softening point and high glass transition temperature (T_g). Chemical structures of a few vinylidene cyanide based copolymers are represented in Figure 23.4 [NAL 95].

In these copolymers, the nitrile group possesses a strong dipole moment of $1.12.10^{-29}$ C.m which causes the formation of hydrogen bonds and dipole interactions in the physical structure. The Nuclear Magnetic Resonance (NMR) ^{13}C spectra reveal that these copolymers are alternated with a head–tail arrangement.

This technique also shows that there is no stereoregularity of successive vinyl ester motifs, contributing to the amorphous structure of copolymers. This amorphous structure is confirmed by studies of x-ray diffraction which, however, reveal a local

order in the glass state, disappearing when the temperature is raised above the glass transition.

Indeed, the dipolar interactions of nitrile groups favor the local order of the amorphous phase. Then, at the crossing of the glass transition, this weak cohesion between macromolecules is destroyed by cooperative molecular motions. This phenomenon causes an endothermal peak on the thermograms recorded by differential enthalpic analysis (DEA).

Orientation of dipole moments in the domains of local order allows electro-active properties specific to VDCN copolymers to be communicated.
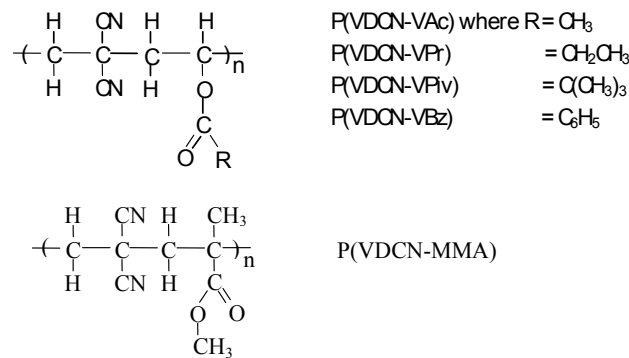
Figure 23.4. *Chemical structures of vinylidene cyanide copolymers: VAc= vinyl acetate, VBz= vinyl benzoate, VPr= vinyl propyonate, VPiv= vinyl pivarate, MMA= methyl methacrylate*

23.3. Electro-active properties of piezoelectric polymers

23.3.1. *Ferroelectricity*

By definition, a crystal, a ceramic or a polymer is ferroelectric if it can present, in the absence of an electric field, a polarization P (C.m^{-2}) which can be inversed by the application of an electric field E (V.m^{-1}) greater than a critical value E_c, called a coercive field.

Ferroelectricity is present in ten classes of crystalline symmetry which do not possess any center of symmetry. In these materials, a weak frequency alternative field with amplitude $E_m > E_c$ produces a hysteresis loop between the electric displacement vector D_i (C.m^{-2}) and the electric field E_i:

$$D_i = \varepsilon_0 E_i + P_i \qquad \text{(with } 1 \leq i \leq 3) \qquad [23.2]$$
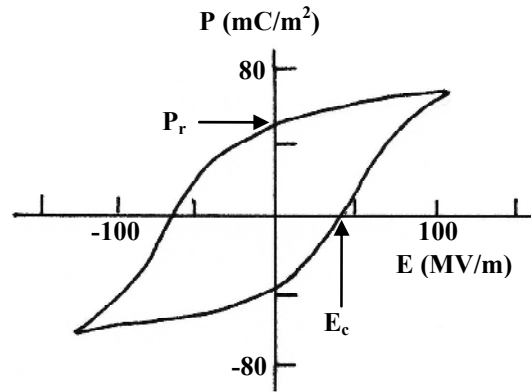
Figure 23.5. *Hysteresis loop of a ferroelectric PVDF*
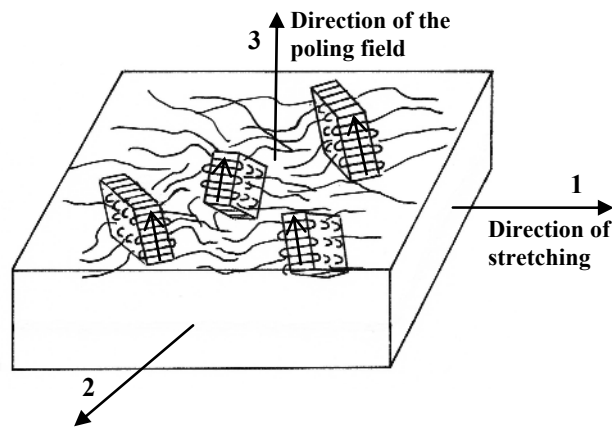
Figure 23.6. *Definition of the tensorial directions for a piezoelectric semi-crystalline polymeric film, the arrows in the crystallites designate their polarization*

The example of a hysteresis loop obtained on a ferroelectric PVDF is represented in Figure 23.5. For a null field, $D = P_r$, where P_r is called the remnant polarization of the material. The values of the index $i = 1, 2$ and 3 correspond to the numbers associated with the three axes represented for a ferroelectric polymeric film in Figure 23.6. The previous section on piezoelectric polymeric materials shows that the application of a thermomechanical orientation on the films permits the optimization of the polarization of crystallites or of the domains of local order in

fluorinated polymers, odd polyamides, and Poly(vinylidene cyanide) copolymers. Thus, the axes at the scale of the film are designated by convention [LOV 83]: (1) for the direction of stretching or the preferred direction of the axis of molecular chains, (2) for the direction in the film plane and perpendicular to (1) and (3) for the direction perpendicular to the film plane corresponding to that of the poling field.

In ferroelectric materials, the polarization appears spontaneously at the microscopic scale, corresponding to the ferroelectric domains in monocrystals, to microcrystals in ceramics and crystallites in polymers. However, these polarized regions generally have a random orientation with respect to each other, such that their sum makes the material non-polarized. The application of an electric field greater than the coercive field is therefore fundamental to obtain a macroscopic polarization.

The ferroelectricity of polymers is due to the presence of permanent dipoles associated with each monomer [LOV 85]. Thus, for odd polyamides, we have described in the previous section that a uniaxial orientation produces an orientation of hydrogen bonds parallel to the film plane. The application of an electric field then causes a 90° rotation of the dipoles. The structure in sheets then passes from an orientation in the film plane to an orientation perpendicular to the film plane, by a simple twist of the chains around their main axis [SCH 92]. The film thus polarized is illustrated in Figure 23.6.

In general, the pole field E greater than E_c allows orienting the dipoles in a direction and thus creates a stable configuration under no external field: each dipole tends to orient itself in the local field created by all the other dipoles [LOV 83]. As shown in Figure 23.6, the polarization resulting from each crystallite is therefore oriented in a preferred manner according to the poling field E. In a volume element dv the polarization P is written as a function of the dipole moments μ_i:

$$\sum \vec{\mu}_i = \vec{P}.dv \qquad [23.3]$$

As in insulating materials, the polarization is related to the electric field by the dielectric susceptibility χ_{ij} (F.m-1) (where χ_{ij} is a second-rank tensor):

$$P_i = \chi_{ij} E_j \qquad [23.4]$$

Both relationships [23.2] and [23.4] allow us to obtain:

$$D_i = \varepsilon_0 E_i + \chi_{ij} E_j = \varepsilon_0 \delta_{ij} E_j + \chi_{ij} E_j = (\varepsilon_0 \delta_{ij} + \chi_{ij}) E_j = \varepsilon_{ij} E_j \qquad [23.5]$$

where $\varepsilon_{ij} = \varepsilon_0 \, \delta_{ij} + \chi_{ij}$ is the dielectric permittivity of the material and $\delta_{ij} = 1$ for $i = j$, $\delta_{ij} = 0$ for $i \neq j$. For most ferroelectrics, $\varepsilon_0 \, \delta_{ij} << \chi_{ij}$ and $\varepsilon_{ij} \approx \chi_{ij}$. In practice, the relative dielectric permittivity $\varepsilon_r = \varepsilon_{ij} / \varepsilon_0$ is commonly used.

23.3.2. *Semi-crystalline polymers: Fluorinated polymers and odd polyamides*

The origin of the polarization in fluorinated polymers and in odd polyamides was much debated for a long time. In particular, different processes were proposed in order to explain the electro-active properties of PVDF in the β-phase: the electret effect and the Maxwell–Wagner–Sillars effect notably. The revelation of the hysteresis loop and dipolar reorientation in fluorinated polymers and in odd polyamides allowed the ferroelectric character of these materials to be shown. The origin of the polarization was therefore attributed to crystalline zones [LOV 83, DAS 91]. Table 23.1 compares the characteristic parameters of PVDF in β-phase and a ferroelectric P(VDF-TrFE) 75-25 with a TGS crystal and a BaTiO$_3$ ceramic. We note that the properties of ferroelectric polymers depend on the implementation conditions of the film (uniaxial or biaxial orientation, temperature, etc.).

In comparison with crystals and ceramics, certain ferroelectric polymers, such as P(VDF-TrFE) copolymers, present a phase transition produced at the Curie temperature (T_c) [FUR 89]. Beyond this temperature, these materials lose their ferroelectric properties and become paraelectric. Depending on the transition order, the remnant polarization P_r, is cancelled in a continuous (second order transition) or discontinuous (first order transition) way. No ferro/paraelectric phase transition is observed in PVDF and odd polyamides.

Ferroelectric materials	E_c (MV/m)	P_r (mC/m²)	T_{fp} (°C)	ε_r (at 20°C)
TGS	1	28	49	50
BaTiO$_3$	0.1 to 2	260	120	1,200
PZT	2.5	140	>300	1,700
PVDF	30 to 100	30 to 60	—	10 to 15
P(VDF/TrFE) 75/25	~ 100	50 to 100	130	~ 10

Table 23.1. *Coercive field, E_c, remnant polarization, P_r, ferro / paraelectric transition temperature, T_{fp}, and relative dielectric permittivity, ε_r, of ferroelectric materials*

23.3.3. *Amorphous Poly(vinylidene cyanide) copolymers*

The electro-active properties of vinylidene cyanide (VDCN) copolymers depend on the dipole moments μ of the constituent motifs, and their concentration N. The obtained values, for example, in the P(VDCN-VAc) copolymer are respectively

$\mu = 19.10^{-30}$ C.m and N $=$ $0.44.10^{28}$ m^{-3}, while in PVDF, they correspond to $\mu = 6.7.10^{-30}$ C.m and N $=$ $18.40.10^{28}$ m^{-3}. The piezoelectric properties are also related to the ability of the dipoles to orient themselves during the application of an electric field E. In amorphous polymers, the orientation of dipoles gets easier as the molecular mobility is high. Thus, the poling process involved heating samples to some high temperature greater to that of the glass transition (T $>$ Tg), applying a high electric field and then cooling the polymer to room temperature with the field applied.

The optimization of the aligning of dipoles depends on the incidence of the polarization temperature and the intensity of the electric field on the relaxation time associated with the molecular mobility. Although the intensity of the electric field must be as high as possible to obtain the best resulting polarization, the value of E is restricted to that which produces the dielectric breakdown. In general, for these amorphous copolymers, the applied electric field is less than 100 MV/m.

The polarization $P_t = N.\mu$ corresponds to the maximal theoretical value which could be obtained in a polymer. However, for the best experimental polarization conditions, the results show that the optimal orientation of the dipoles with respect to the poling field gives a remnant polarization P_r much lower than P_t. For most polymers, the measured remnant polarization corresponds to an average value of the ratio $(P_r/P_t) \approx 30\%$. This ratio can, depending on the polymer, clearly diverge from the average value; thus, for example, the ratio P_r/P_t corresponds to a value of about 30 to 42% for PVDF, while it reaches 60% for P(VDCN-VAc) with, for this amorphous copolymer, $P_r = 50$ mC/m^2. The remnant polarization values of VDCN copolymers are reported in Table 23.2 [NAL 95].

Copolymers	T_g (°C)	ε_r (at 20°C)	$\Delta\varepsilon_r$ (at T_g)	P_r (mC/m²)
P(VDCN-VAc)	178	5.6	120	35
P(VDCN-VBz)	184	5.6	115	21
P(VDCN-VPr)	176	5.8	85	28
P(VDCN-VPiv)	172	5.8	100	33
P(VDCN-MMA)	146	5.4	30	12

Table 23.2. *Glass transition obtained by AED , Tg, dielectric constant at 20°C and 10 Hz, ε_r, intensity of the dielectric relaxation at T_g, $\Delta\varepsilon_r$, and remnant polarization, P_r, of vinylidene cyanide copolymers*

In semi-crystalline polymers, the polarization of crystallites is not modified for temperatures higher than glass transition. For this reason, PVDF ($T_g \approx -35$°C) can be used up to temperatures of 80 to 100°C. In amorphous copolymers, the electro-active properties are stable until temperatures situated around the glass transition temperature zone, at which point the increase in the molecular mobility causes a loss

of the orientation of dipoles. It is interesting to note that the value of T_g in amorphous copolymers reported in Table 23.2 can reach 170 to 180°C. Furthermore, the intensities of the dielectric relaxation $\Delta\varepsilon$ which are indicated in this table define the amplitude of the dielectric constant hop to the temperature zone crossing of the glass transition (T_g). Thus, the high value of $\Delta\varepsilon$ reported for vinylidene cyanide copolymers reveals cooperative molecular motions with large amplitude at the crossing of T_g.

23.3.4. *Influence of chemical composition and physical structure on the electro-active properties of polymers*

The chemical composition of polymers modifies their ferroelectric properties. Furukawa [FUR 89] revealed that in fluorinated copolymers the unit rate of trifluoroethylene has an influence on the remnant polarization. The maximum remnant polarization $P_r = 100$ mC/m^2 is reached for P(VDF-TrFE) 80-20, while it is of the order of 60 mC/m^2 in the PVDF homopolymer. We must note that the increase in the rate of TrFE motifs would tend to reduce the dipole moment of a macromolecule because the dipole moment associated with the TrFE motif is less than that of the vinylidene (VDF) motif. The results show that rates of TrFE less than 20% molar cause a reduction of the remnant polarization. This evolution is attributed to a decrease in the crystallinity rate. Moreover, it is for a TrFE rate greater than 50% molar that the ferroelectrics properties appear more clearly, because the conformational disorder leads to the outbreak of new crystalline phases.

Odd polyamides	PA 11	PA 9	PA 7	PA 5
Density of dipoles 10^{-30} C.m /100Å^3	4.29	4.93	6.59	9.41
P_r (mC/m²)	56	68	86	125
E_c (MV/m)	64	75	80	100

Table 23.3. *Density of dipoles, remnant polarization and coercive field in odd polyamides [MEI 93]*

In odd polyamides, the remnant polarization and the coercive field are both directly proportional to the density of dipoles in the material corresponding to the density of amide groups (Table 23.3). The shortening of paraffin sequences situated between amide groups increases the cohesion energy of crystalline regions. Thus, the increase in the coercive field is associated with an increase in the density of dipoles and therefore in the number of hydrogen bonds [MEI 93].

Generally, in semi-crystalline polymers, since the electro-active properties are mainly related to the nature of the crystalline phase, the improvement of the macroscopic polarization is obtained by processes of thermal processing or mechanical stretching, which either allows the crystallinity rate to increase, or to increase the relative orientation of crystallites.

In amorphous VDCN copolymers, local order plays a major role on the electro-active properties. The increase in the remnant polarization occurs if a local order exists in the amorphous polymers, or if it is produced by a thermomechanical orientation. Indeed, the orientation causes an increase in intermolecular dipolar interactions and facilitates the densification of the arrangement of macromolecules. These zones of local order thus generated will give rise to a larger polarization P_r.

23.3.5. *Protocols of polarization*

Several polarization protocols of polymeric films have been used since the discovery of the ferroelectric properties of these materials. The first method, proposed by H. Kawaï for the polarization of PVDF films, consisted of applying a continuous electric field of about 30MV/m at 90°C for a relatively long time ($\approx 10^3$s), then cooling the film under an electric field down to room temperature [KAW 69].

A method for industrial use was also developed: Corona polarization [BAU 96]. This method permits a polarization to be made at room temperature in short times (≈ 10s), gets rid of the breakdown phenomena of films and thus polarizes very large film surfaces. The device is composed of a point situated a few centimeters from the film surface, with a very high potential (20 kV) producing air ionization. A grid placed between the point and the film surface is brought to an intermediary potential (10 kV) permitting the field to homogenize at the film surface and to fit the potential for its surface. The charges thus drained towards the film surface create a strong electric field (of a few hundred MV/m) which causes the orientation of the dipoles of the crystalline phase.

Another method, particularly developed at the Franco-German Institute of Saint Louis (ISL) [BAU 94], consists of applying a low frequency alternative electric field on an initially metallized film. The gradual increase in the poling field allows, when E is greater than the coercive field, the hysteresis loop between the polarization and the electric field to be reached. When the poling field is reduced to zero, the film possesses a permanent polarization which is very stable over time.

23.3.6. *Piezoelectricity*

Piezoelectricity is the property of certain materials to charge themselves electrically when they are submitted to a mechanical stress (a direct piezoelectric effect) or to get deformed under the action of an electric field (converse piezoelectric effect) [NYE 85]. This effect, only present in insulating materials, is equivalent to the outbreak of charges with opposite signs on both sides of the film. At the molecular level, this effect is due to the non-coincidence of centers of gravity with positive and negative charges.

The direct piezoelectric effect causes a linear relationship between the X_{ij} (N.m^{-2}) components of the second-rank tensor, representing the stress state applied to the piezoelectric material and the resulting charge density (electric displacement) D_i which is produced at constant electric field E and temperature T:

$$D_i = d_{ijk} X_{jk} \qquad \text{(with } 1 \leq i, j, \text{ and } k \leq 3) \qquad \text{[23.6]}$$

The three components of the polarization are therefore related to the nine X_{ij} components of the stress, by the 27 constant piezoelectric coefficients d_{ijk} (C.N^{-1}), a third-rank tensor.

The converse piezoelectric effect is the thermodynamic consequence of the direct effect. In the converse effect, there is a linear relationship between the components of the vector E_i, intensity of the electric field applied to the material, and the tensor components of the strain S_{ij} characterizing the change of the material dimensions (they contract or expand). Thus, at constant stress and temperature:

$$S_{ij} = d_{kij} E_k = d_{ijk}^t E_k \qquad \text{(with } 1 \leq i, j, \text{ and } k \leq 3) \qquad \text{[23.7]}$$

where the exponent t indicates the transposed matrix. The units of the converse piezoelectric coefficients are (m.V^{-1}). The piezoelectric coefficients for the direct and converse piezoelectric effects are thermodynamically identical, i.e. $d_{direct} = d_{inverse}$; they can be either positive or negative. Let us note that the sign of the charge D_i and of the strain S_{ij} resulting from the piezoelectric effect depends on the direction of the mechanical and electric fields respectively. Usually, the piezoelectric coefficient measured in the direction of applied electric field is designated as the longitudinal coefficient, whilst that measured in the direction perpendicular to the electric field is called the transverse coefficient. The coefficients having indices $i \neq j$ represent the shear components of strain and stress tensors.

The piezoelectricity of polymers is caused by the biphasic character of these materials. Thus, the specificity of the piezoelectric properties is attributed to the

existence of an intrinsic polarization of crystalline domains associated with the mechanical adaptation of the amorphous phase.

According to the generalized form of Hooke's law, a solid submitted to a stress X_{jk} lower than the sufficiently weak elasticity and intensity limit, will be subjected to a strain S_{ij} in the linear approximation, such as:

$$S_{ij} = s_{ijkl} X_{kl} \qquad\qquad \text{(with } 1 \leq i, j, k \text{ and } l \leq 3) \qquad\qquad [23.8]$$

where s_{ijkl} (m^2.N^{-1}) represents the elastic compliance of a fourth-rank tensor.

The inverse relationship $X_{ij} = c_{ijkl} S_{kl}$ defines elastic stiffness tensor c_{ijkl} (N.m^{-2}) of the material. The coefficients of these two tensors are related by the relationship: $s_{ijkl} \cdot c_{klmn} = c_{ijkl} \cdot s_{klmn} = \delta_{im} \cdot \delta_{jn}$.

The piezoelectric effect is present in 20 classes of crystalline symmetry which do not possess any center of symmetry. Ferroelectricity is therefore not a condition required for the existence of piezoelectricity. Indeed, piezoelectricity can exist at temperatures greater than the ferro/paraelectric transition, or in non-ferroelectric materials such as quartz.

23.3.7. *Reduction of the number of independent coefficients – Matrix notation*

In general, stress and strain are represented by symmetric tensors ($X_{ij} = X_{ji}$ and $S_{ij} = S_{ji}$), causing coefficients d_{ijk} symmetric in j and k on the piezoelectric tensor: $d_{ijk} = d_{ikj}$. The number of independent piezoelectric coefficients is thus reduced from 27 to 18. Furthermore, the symmetry of stress and strain tensors also reduces the number of elasticity and rigidity coefficients from 81 to 36. It is therefore possible to use a more concise notation to write the coefficients of piezoelectric, elasticity and rigidity tensors, known as matrix notation [NYE 85]. In this matrix notation, the second and the third index of d_{ijk}, as well as both indices of X_{jk} are reduced to only one index which varies from 1 to 6, depending on the relation: the pairs of indices ii = 11, 22, 33 are respectively replaced by m = 1, 2, 3, and the pairs of mixed indices ij = 23 or 32, 13 or 31, 12 or 21 are respectively replaced by m = 4, 5, 6. Equations [23.6], [23.7] and [23.8] are respectively written in the following matrix format:

$$D_i = d_{im} X_m \qquad\qquad\qquad\qquad [23.9]$$

$$S_m = d_{im} E_i \qquad\qquad\qquad\qquad [23.10]$$

$$S_m = s_{mn} X_n \qquad\qquad\qquad\qquad [23.11]$$

where i = 1, 2, 3 and m, n = 1, 2, …, 6. It is important to note that the matrices s, d, X and S in their reduced notation do not transform as tensors when the coordinate system is changed.

23.3.8. *Piezoelectric constitutive equations*

A formalism presenting the coupling between the thermal, elastic and electric parameters of a material was introduced based on thermodynamic principles [MIT 76, MAS 50]. Thus, the choice of several thermodynamic potentials and independent variable combinations allowed a series of eight piezoelectric constitutive equations to be obtained for an isothermal process which, written in matrix notation, reduce to:

$$S_m = s_{mn}^{T,E} X_n + d_{im}^{T,X} E_i \quad \text{[23.12]} \qquad X_m = c_{mn}^{T,D} S_n - h_{im}^{T,S} D_i \quad \text{[23.16]}$$

$$D_i = d_{im}^{T,E} X_m + \varepsilon_{ij}^{T,X} E_j \quad \text{[23.13]} \qquad E_i = -h_{im}^{T,D} S_m + \beta_{ij}^{T,S} D_j \quad \text{[23.17]}$$

$$X_m = c_{mn}^{T,E} S_n - e_{im}^{T,S} E_i \quad \text{[23.14]} \qquad S_m = s_{mn}^{T,D} X_n + g_{im}^{T,X} D_i \quad \text{[23.18]}$$

$$D_i = e_{im}^{T,E} S_m + \varepsilon_{ij}^{T,S} E_j \quad \text{[23.15]} \qquad E_i = -g_{im}^{T,D} X_m + \beta_{ij}^{T,S} D_j \quad \text{[23.19]}$$

with $1 \leq i$ and $j \leq 3$, and $1 \leq m$ and $n \leq 6$. The superscripts in equations [23.12] – [23.19] indicate the variables which are maintained constant.

According to equations [23.12] and [23.13], the pure piezoelectric effect of deformation (of electric charge) is exclusively obtained under no stress conditions (no electric field); e, g and h are piezoelectric tensors; c is the calorific capacitance and β is the inverse dielectric susceptibility (= χ^{1}). The thermodynamics of piezoelectric materials also reveals that the piezoelectric coefficients of the same type are thermodynamically equivalent: $d^X = d^E$, $g^D = g^X$, $e^S = e^E$ and $h^D = h^S$, their superscripts are usually omitted. Moreover, the piezoelectric tensors' coefficients are mutually related by the following relationships:

$$d_{im} = e_{in} s_{nm}^E = \varepsilon_{ij}^X g_{jm} \qquad \text{(m.V}^{-1}\text{ or C.N}^{-1}\text{)} \qquad \text{[23.20]}$$

$$e_{im} = d_{in} c_{nm}^E = \varepsilon_{ij}^S h_{jm} \qquad \text{(C.m}^{-2}\text{ or N.V}^{-1}\text{.m}^{-1}\text{)} \qquad \text{[23.21]}$$

$$g_{im} = h_{in} s_{nm}^D = \beta_{ij}^X d_{jm} \qquad \text{(m}^2\text{.C}^{-1}\text{ or V.m.N}^{-1}\text{)} \qquad \text{[23.22]}$$

$$h_{im} = g_{in} c_{nm}^{D} = \beta_{ij}^{X} e_{jm} \qquad \text{(N.C}^{-1} \text{ or V.m}^{-1}) \qquad [23.23]$$

Thus, d_{im} is designated as the strain or the electric charge coefficients, e_{im} as the electric charge or the stress coefficients, g_{im} as the strain or the voltage coefficients and h_{im} as the stress or the voltage coefficients. Consider, as an illustration, the difference between g and d coefficients, while omitting matrix indices for simplicity. Equation $D = d.X$ gives the piezoelectric charge measured on a sample connected in short circuit, allowing the flow of charges in the external circuit. If, on the other hand, the sample is placed in an open circuit, the charges will accumulate at the surface of the sample and will produce an electric field E through the sample. This electric field depends on the capacitance (permittivity) of the sample (charge = capacitance.voltage) being related to the stress by: $E = -g . X$ with $g = d/\varepsilon$.

23.3.9. *Comparison of piezoelectric properties*

Let us take for example PVDF, one of the polymeric materials much used in applications, in which only 5 of its piezoelectric coefficients are non-zero, considering its symmetry [NYE 85]:

$$d_{ij} = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{24} & 0 & 0 \\ d_{31} & d_{32} & d_{33} & 0 & 0 & 0 \end{bmatrix} \qquad [23.24]$$

d_{31}, d_{32}, d_{33} associate a longitudinal stress, depending on the axes 1, 2, 3, to a polarization in the direction (3). Both other coefficients are related to shear effects. When the film is isotropic in its plane (biaxially oriented or unoriented): $d_{31} = d_{32}$, and $d_{15} = d_{24}$.

Ferroelectric materials	d_{31} (10^{-12} C/N)	e_{31} (10^{-2} C/m²)	g_{31} (10^{-3} V.m/N)	h_{31} (10^{7} V/m)	k_{31}
PVDF	20	6.0	174	53	0.10
P(VDF/TrFE)(55/45)	25	3.0	160	19	0.07
P(VDF/TrFE) (75/25)	10	2.0	110	22	0.05
P(VDCN/VAc)	6	2.7	169	76	0.06
PZT	110	920	10	87	0.31

Table 23.4. *Comparison of piezoelectric properties of polymers and nonorganic materials [NAL 95]*

Table 23.4 compares the physical properties of the commercially available piezoelectric polymers with the properties of a typical piezoelectric ceramic, PZT [NAL 95]. We note that the piezoelectric constants d_{31} of all polymers are relatively weak in comparison to the highest values of PZT. However, this is compensated by a dielectric constant ε_r which is weaker in polymers (Tables 23.1 and 23.2). Thus, the voltage generated per unit stress, which is called g_{31}, is higher in polymers than in other materials, which gives them a better sensitivity during the application of a force (stress).

The electromechanical coupling factor k_{ij} is introduced to directly estimate in a material the conversion efficiency from one form of energy to another. The coupling factor k is therefore defined as a function of the direct or converse piezoelectric effect by the relationships:

$$k^2 = \frac{Mechanical\ energy\ converted\ to\ electrical\ energy}{Total\ input\ mechanical\ energy} \qquad [23.25]$$

$$k^2 = \frac{Electrical\ energy\ converted\ to\ mechanical\ energy}{Total\ input\ electrical\ energy} \qquad [23.26]$$

23.4. Piezoelectricity applications

23.4.1. *Transmitting transducers*

Transmitting transducers correspond to piezoelectric applications where the electrical energy provided to dielectric (free remainder to become deformed) is by unit volume (to simplify, the indices are omitted):

$$W_f = \frac{1}{2}\varepsilon^X E^2 \qquad [23.27]$$

where ε^X is the permittivity of the free dielectric and E the applied electric field. The mechanical energy converted by piezoelectric effect of the electrical energy is by unit volume:

$$W_m = \frac{1}{2}s^E S^2 \qquad [23.28]$$

where s^E is the elastic constant at given electric field and S the strain. By piezoelectric effect, the deformation is proportional to the applied field $S=d.E$. The supplied energy W_f is therefore split into two parts:

$$W_f = W_{él} + W_m = \frac{1}{2}\varepsilon^S E^2 + \frac{1}{2}s^E d^2 E^2 \qquad [23.29]$$

where ε^S is the permittivity of the clamped dielectric. So:

$$W_f = \frac{1}{2}\varepsilon^S\left(1+\frac{s^E d^2}{\varepsilon^S}\right)E^2 = \frac{1}{2}\varepsilon^S\left(1+k^2\right)E^2 \qquad [23.30]$$

k^2 therefore represents the fraction of supplied electrical energy which is transformed into mechanical energy [23.26]. The electromechanical coupling factor can be obtained from measured d-constant as follows:

$$k = d\sqrt{\frac{s^E}{\varepsilon^S}} \qquad [23.31]$$

For PVDF, k^2 is of the order of 5.10^{-2}, whereas for polycrystalline ferroelectrics, the coupling factor ranges between 25.10^{-2} and 40.10^{-2}. Although the coupling factor of PVDF is weaker than that of ferroelectric ceramics, the convertible mechanical energy is potentially of the same order of magnitude: indeed, the maximum electric fields applicable to PVDF are greater than those supported by ceramics (because coercive fields are higher in PVDF at room temperature, and the weak thicknesses achievable in polymers facilitate the thermal dissipation). Thus, for:

– PVDF: $E_{max} = 10^7$ V.m^{-1} and $\varepsilon^X = 10^{-10}$ F.m^{-1} gives $W_{fmax} = 5000$ J.m^{-3};

– PZT: $E_{max} = 3.10^5$ V.m^{-1} and $\varepsilon^X = 10^{-8}$ F.m^{-1} gives $W_{fmax} \approx 500$ J.m^{-3}.

The maximal energy we can supply to PVDF is therefore about 10 times higher than that admissible by a PZT ceramic, for which the electromechanical conversion efficiency is about 10 times stronger. Other polymers, P(VDF-TrFE) and P(VDNC/VAc) have ferroelectric properties comparable (Table 23.4) to that of PVDF. If we consider that the acoustic matching of the propagation media (air, water, biological tissues) is better for polymers than for PZT and certain characteristics intrinsic to polymers (soft, light, and easy to manufacture into large sheets and cut or bend into complex shapes) can be dominating, it appears that ferroelectric polymers take an interesting place in being complementary to PZT in specific applications, as in the domains of high fidelity loudspeakers and earphones, underwater acoustic hydrophones and probes for medical ultrasound.

23.4.2. *Piezoelectric sensors*

In the domain of application of piezoelectric sensors, the evaluation of the specificity of both types of polymeric and ceramic materials is made, like in the previous section, by undertaking a study based on PVDF and PZT.

As can be shown from Table 23.4, for all piezoelectric coefficients d, where (to simplify) the indices are omitted, a charge freed during the application of the same stress will be 10 times weaker in PVDF than in PZT: $d_{(PVDF)} \approx 10$ to 20 pC.N^{-1} and $d_{(PZT)} \approx 100$ at 300 pC.N^{-1}.

The permittivity ε of PVDF is about 100 times weaker than that of PZT; the electric field generated within the dielectric, for a given stress, is also higher for PVDF. Indeed, the piezoelectric constant, $g = d / \varepsilon$, shows that $g_{(PVDF)} \approx 10$ at 20.10^{-2} V.m.N^{-1} and $g_{(PZT)} \approx 1$ to 3.10^{-2} V.m.N^{-1}. Thus, for a sensitivity s_e given in voltage by unit stress, the thickness $é$ of a PVDF film can be 10 times smaller than that of PZT since: $s_e = g \,.\, é$ (V.N^{-1}.m^2).

The merit factor, $M = W/v$, of a low frequency sensor, particularly in the case of hydrophones, is defined as the electrical energy available by unit volume v for a unit stress. This merit factor is favorable to PVDF in comparison with PZT:

$$M = \frac{1}{2} \frac{s_e^2 \, C}{v} = \frac{1}{2} g^2 \varepsilon = \frac{1}{2} g \,.\, d \qquad\qquad [23.32]$$

where C is the electrical capacitance of the film, thus:

$g_{(PVDF)} \,.\, d_{(PVDF)} \approx g_{(PZT)} \,.\, d_{(PZT)} \approx 1$ at 9.10^{-12} J.m^{-3}/N.m^{-2}.

As in the case of transmitting transducers, PVDF cannot claim to replace PZT type ceramics, but covers applications such as light active membranes (microphones), weak dimension pressure probes (shockwave chronography), large band probes for ultrasound echography, and high dimension hydrophones required for very low frequencies.

23.5. Transducers

23.5.1. *Principle*

Electroacoustic transducers are made up of piezoelectric polymer films metallized on both sides. In the audio frequency range, the application of an alternating voltage between the metallized sides generates a surface variation by

transverse piezoelectric effect, to which a vibration of the film corresponds. If the frequency imposed by the voltage is sufficiently high, the film vibrates following its thickness direction at high frequency, producing ultrasounds. Electroacoustic transducers such as headphones, speakers and ultrasonic generators all work according to this principle. Thus, for the same applied voltage, a high piezoelectric constant causes a large displacement (deflection), and for a large Young's modulus, the film gives a stronger output force during the vibration. Vice versa, a pressure difference in the front and rear sides of the piezoelectric film leads to a surface variation which causes the outbreak of an electric voltage between electrodes. This type of functioning is used in sensors devices: microphones, pressure probes, etc.

Piezoelectric polymers challenge ceramics with their large surfaces, weaker density, better acoustic matching to aqueous media and lower price. Furthermore, they present a strong advantage; they can be thermoformed according to the shapes of any surfaces whose geometries could not be made before, to constitute sensors and transducers of specific shape: spheres and segments of a sphere, pistons, surfaces adapting themselves well to that of the support, etc.

23.5.2. *Electroacoustic transducers*

The first commercial applications of piezoelectric polymeric films were electroacoustic transducers such as high-frequency loudspeakers (tweeters), stereophonic headphones and microphones, [RAV 81] which are distinguished from usual transducers by an active membrane. The piezoelectric polymeric films are well fitted for this type of acoustic transducer which possesses a wide range in frequency. Indeed, the characteristics of these polymers allow an implementation in the form of a thin film (1 – 300 μm), with low mechanical stiffness. In 1974, The Pioneer Company thus developed an omni-directional tweeter up to 20 kHz, composed of a piezoelectric PVDF film. The realization of numerous acoustic transducers possessing piezoelectric polymeric films has been described in several articles [WAN88]. The small thickness of films allows promising applications such as a transparent loudspeaker composed of a P(VDCN/VAc) film with the aspect of a sheet of paper.

23.5.3. *Characteristics of ultrasonic transducers*

The development of piezoelectric polymers applications in the domain of ultrasonic transducers is very promising. The transducers realized cover a wide range of frequency from 10 kHz to 100 Mhz, such as hydrophones, acoustic probes for non-destructive testing and probes for medical echography. Table 23.5 compares a few physical properties of these materials with those of piezoelectric ceramics

much used in ultrasonic transducers. Ferroelectric polymers present several advantages in comparison with ceramics:

– these soft materials are characterized by an acoustic impedance (about 4.10^6 $kg.m^{-2}.s^{-1}$) near to that of water and the human body, allowing more complete energy transfer and a weaker reflection and distortion of the wave at the transducer interface;

– the large mechanical loss of polymers permits short pulses with a high distance resolution to be obtained;

– the implementation of polymers permits the form to be adjusted, in order to improve the ultrasound wave focus; a better resolution of the direction and the analyzed zone is thus obtained;

– the biocompatibility of these materials with human tissues is favorable to medical applications.

Ferroelectric material	Density ρ (10^3 kg/m^3)	Sound velocity (10^3 m/s)	Coupling factor k_{31}	Mechanical loss $\tan \delta e$	Acoustic impedance Z (10^6 kg/m^{2}s)
PVDF	1.78	3.0	0.20	0.13	4.0
P(VDF/TrFE) 75/25	1.88	2.0	0.30	0.05	4.5
P(VDCN/VAc)	1.20	4.5	0.28	0.02	3.0
PZT	7.5	83.3	0.64	0.002	30

Table 23.5. *Electromechanical properties of polymeric and ceramic materials for ultrasonic transducers*

23.5.4. *Hydrophones*

One of the original applications of ferroelectric polymers was as an acoustic probe immersed in water. Polymeric films which make up hydrophones are active materials mainly characterized by piezoelectric constants which depend on the type of application, the structure of the transducer, the frequency band used, and the exposition conditions of the film in its environment.

Let us first consider the hydrophone in its sensor mode, when it operates as a recepting transducer, where the piezoelectric film is deformed under the effect of acoustic wave pressure. At the lowest frequencies, the piezoelectric hydrostatic constant in voltage g_{3h} is used, whilst at highest frequencies, the piezoelectric constant in voltage g_{33} is dominating. Indeed, at sufficiently low frequencies, the

size of the active material can be considered small in comparison with the acoustic wavelength, so that the acoustic pressure is identical depending on the three axes of the hydrophone. In these conditions, the output signal of the hydrophone is a function of the hydrostatic mode associated with the piezoelectric constant in voltage g_{3h}. This constant is defined as the superposition of active modes according to the three axes:

$$g_{3h} = g_{31} + g_{32} + g_{33} \qquad\qquad [23.33]$$

where g_{3h} corresponds to the electric excitation produced according to the three axes and h indicates a hydrostatic mode. For piezoelectric ceramics and piezoelectric copolymers, the modes (3,1) and (3,2) are identical:

$$g_{3h} = 2g_{31} + g_{33} \qquad\qquad [23.34]$$

As for the hydrophone in the transmitting mode, at high frequencies the piezoelectric effects following the thickness are associated with the dominating electric charge constant d_{33}, whilst d_{3h} is used at low frequencies.

In PZT, the negative values of the constants g_{31} and g_{32} and the positive values of g_{33} give a low g_{3h} in comparison with the pure (3,3)-mode excitation, causing a weak hydrostatic-mode hydrophone. For the piezoelectric homopolymer, PVDF, the mode constants (3,1) and (3,2) are different because of the stretching and poling processes involved during its implementation. These characteristics communicate to the PVDF a relatively high and useful hydrostatic receiving sensitivity, thus favoring the development of a hydrophone in hydrostatic-mode.

Planar hydrophones were the first hydrostatic probes made with a PVDF film. In the eighties, this type of device was then improved by placing a stiffener either behind a single sheet or between two sheets of ferroelectric polymers. The stiffening layers were thick plates of epoxy-loaded graphite and aluminum. The reason for the addition of a stiffener to the hydrostatic transducer design was to improve low frequency response. However, this rigid membrane tends to block the polymeric film laterally, in such a way that the (3,1) and (3,2) modes are restricted [WAN 88].

The cylindrical hydrophone is probably the simplest device which operates in hydrostatic mode. This type of probe, made for example with a piezoelectric copolymer, is of cylindrical shape [NAL 95]. These cylinders can have a nominal external diameter ranging between 0.64 and 2.54 cm, and a length which can reach 30 cm. For a nominal wall of thickness 0.5 to 1.3 mm, the sensitivity reached is -202 to -194 dB, corresponding to 1 V.μPa^{-1}. The performances and the characteristics thus obtained are due to the properties of active materials, but for numerous uses of these hydrophones, the cylinder must be protected by a coating.

The development of hydrophones is mainly made in the domain of excitation modes associated with the coefficients g_{33} and g_{3h}. However, more recent research has been undertaken for the conception of a probe possessing a high gain in the acoustic detection of mode (3,1) [BHA93]. This transducer is made up of a ferroelectric polymeric film tightened by springs along the axis (3,1).

23.5.5. *Probes for Non-Destructive Testing (NDT)*

Piezoelectric polymer-based transducers are also developed in a wide domain of ultrasounds for non-destructive testing (NDT) in industry. PVDF ultrasonic probes have shown that they are characterized by weak noise and a wide band, permitting measurements on metallic or non-metallic pieces to be made [CHA 88]. In the aeronautic domain, it has been shown that this type of probe is also suitable for the testing of composite materials.

In general, the effect of the devices that have been made is that, during tests in which the penetration depth of the probe is essential, piezoelectric ceramics are preferable, whereas when good resolution is preferred, ferroelectric polymers are chosen. Both of these materials can therefore be used in a complementary way in the conception of probes, where the receiving transducers are composed of PVDF and the transmitting transducers are made with PZT [FOS 81].

23.5.6. *Biomedical transducer applications*

The biomedical applications of ferroelectric polymers mainly use their electromechanical transduction properties for the measurements of dynamic pressure during the flow of fluid, heartbeats and contact pressure on soft tissue [GAL 88]. Their low acoustic impedance and their high mechanical losses compared to piezoelectric ceramics imply, for example in PVDF transducers, that the frequency responses are approximately constant in fairly large utilization bands. For thicknesses ranging between 6 and 110μm, the thickness-mode resonance frequencies between 160 kHz and 10 Mhz are achievable. Moreover, a PVDF hydrophone will not perturb the acoustic field and will register rapid dynamic behavior in pressure, as required. These ferroelectric sensors are implemented mainly for external measurements in the form of flexible bands or as implanted sensors applied to pulmonary and cardiovascular domains [MAR 82]. Systems which produce images in real time and which are composed of piezoelectric polymeric films are undergoing an important development in the domain of diagnosis by ultrasound. This type of transducer is especially developed to observe the surface of human organs.

23.6. Conclusion

The potential of piezoelectric polymer applications is great. These polymers have been introduced in numerous sensors and actuators in several domains: medical instrumentation, robotics, electroacoustics and ultrasonic transducers. One of the emerging domains is that of the biomedical world, in which polymers are studied as actuators with the idea of applying them as artificial muscles, medical robots for diagnosis and microsurgery, or implanted to stimulate the tissues.

The development of applications using piezoelectric polymers is conditioned by the improvement of their ability to get integrated into a system, and to meet more and more drastic specifications concerning piezoelectric activity and performance at temperature. The study of the relationship between structure and properties has allowed the development of several semi-crystallins or amorphous polymers owning ferroelectric properties adapted to the realization of new powerful sensors and actuators. On this basis, the investigations are pursued in the domain of the synthesis of materials possessing a high dipole concentration and good electromechanical properties. Indeed, although PVDF and P(VDF-TrFE) possess relatively high piezoelectric responses, these materials have a low relative deformation ($\approx$ 0.1%) and a sensitivity reduced to external stimulations. Recently, a new class of ferroelectric polymers was developed [BAU05], by introducing a monomer, the chlorofluoroethylene (CFE) which is copolymerised with VDF-TrFE to constitute poly(vinylidene-trifluoroethylene-1,1-chlorofluoroethylene fluoride) terpolymer P(VDF-TrFE-CFE). This terpolymer is a ferroelectric relaxor which possesses a high electrostrictive effect with a relative strain change higher than 7% (40% for the muscle) associated with a relatively high modulus of the order of 0.3 GPa (0.8 MPa for the muscle). These properties confer promising electroactive functions on this terpolymer as a sensor or an actuator.

23.7. Bibliography

[BAU 94] BAUER F., "High pressure applications of ferroelectric polymers", *Proceedings 8th International Symposium on Electrets*, IEEE 94CH3443-9, p. 617–622, 1994.

[BAU 05] BAUER F., "Ferroelectric relaxor terpolymers: properties and potential applications", *Proceedings 12th International Symposium on Electrets*, IEEE 05CH37679, p. 117–120, 2005.

[BAU 96] BAUER S., "Poled polymers for sensors and photonic applications", *J. Appl. Phys.*, vol. 80 no. 10, p. 5531–5557, 1996.

[BHA 93] BHAT J.J., THOMSON T.T., SASEENDRAN PILLAI P.R., "Development of (3,1) drive low-frequency piezofilm hydrophones with improved sensitivity", *J. Acoust. Scoc. Am.*, vol. 94, p. 3053–3056, 1993.

[CHA 88] CHANG C., SUN C.T., "A new sensor for quantitative acoustic emission measurement", *J. Acoust. Emission*, vol. 7, p. 21–29, 1988.

[CHE 95] CHEN Q.X., PAYNE P.A., "Industrial applications of piezoelectric polymer transducers", *Meas. Sci. Technol.*, vol. 6, p. 249–267, 1995.

[DAS 91] DAS-GUPTA D.K., "Pyroelectricity in polymers", *Ferroelectrics*, vol. 118, p. 165–189, 19991.

[FOS 81] FOSTER F.S., PATTERSON M.S., HUNT J.W., "The conical scanner: a two transducer ultrasound scatter imaging technique", *Ultrasonic Imaging*, vol. 3, p. 62–82, 1981.

[FUR 89] FURUKAWA T., "Ferroelectric properties of vinylidene fluoride copolymers", *Phase Transitions*, vol. 18, p. 143–211, 1989.

[GAL 88] GALLETTI P.M., DEROSSI D., DEREGGI A.S., *Medical Applications of Piezoelectric Polymers*, Gordon & Breach, New York, 1988.

[KAW 69] KAWAI H., "The piezoelectricity of poly (vinylidene fluoride)", *Jpn. J. Appl. Phys.*, vol. 8, p. 975–976, 1969.

[KEP 92] KEPLER R.G., ANDERSON R.A., "Ferroelectric polymers", *Advances in Physics*, vol. 41, p. 1–57, 1992.

[LOV 83] LOVINGER A.J., "Ferroelectric polymers", *Science*, vol. 220, no. 4602, p. 1115–1121, 10 June 1983.

[LOV 85] LOVINGER A.J., "Recent developments in the structure, properties and applications of ferroelectric polymers", *Jpn. J. Appl. Phys.*, vol. 24, Supplement 24–2, p. 18–24, 1985.

[MAR 82] MARCUS M.A., "Ferroelectric polymers and their applications", *Ferroelectrics*, vol. 40, p. 29–41, 1982.

[MAS 50] MASON W.P., *Piezoelectric Crystals and their Applications in Ultrasonics*, Van Nostrand, New York, 1950.

[MAT 84] MATHUR S.C., SCHEINBEIM J. I., NEWMAN B.A., "Piezoelectric properties and ferroelectric hysteresis effects in uniaxially stretched nylon-11 films", *J. Appl. Phys.*, vol. 56, no. 9, p. 2419–2425, 1984.

[MEI 93] MEI B.Z., SCHEINBEIM J.I., NEWMAN B.A., "The ferroelectric behavior of odd-numbered nylons", *Ferroelectrics*, vol. 144, p. 51–60, 1993.

[MIT 76] MITSUI T., TATSUZAKI I., NAKAMURA E., *An Introduction to the Physics of Ferroelectrics*, Gordon & Breach, London, 1976.

[MIY 80] MIYATA S., YOSHIKAWA M., TASAKA S., KO M., "Piezoelectricity revealed in the copolymer of vinylidene cyanide and vinylacetate", *Polymer J.*, vol. 12, no. 12, p. 857–860, 1980.

[NAL 95] NALWA H.S., *Ferroelectric Polymers*, Marcel Dekker Inc., New York, 1995.

[NEW 90] NEWMAN B.A., KIM K.G., SCHEINBEIM J.I., "Effect of water content on the piezoelectric properties of nylon 11 and nylon 7", *J. Mater. Sci.*, vol. 25, p. 1779–1783, 1990.

[NEY 85] NEY J. F., *Physical Properties of Crystals*, Oxford University Press, Oxford, 1985.

[RAV 81] RAVINET P., GUILLOU D., MICHERON F., "Transducteurs électroacoustiques à dome sphérique de polymère piézoélectrique thermoformé", *Revue Technique THOMSON-CSF*, vol. 13, no. 1, p. 5–42, March 1981.

[SCH 92] SCHEINBEIM J.I., LEE J.W., NEWMAN B.A., "Ferroelectric polarization mechanisms in nylon 11", *Macromolecules*, vol. 25, p. 3729–3732, 1992.

[SER 80] SERVET B., BROUSSOUX D., MICHERON F., BISARO R., RIES S., MERENDA P., "Phases cristallines orientées du poly(fluorure de vinylidène) et leurs propriétés piézoélectriques", *Revue Technique THOMSON-CSF*, vol. 12, no. 4, p. 761–793, December 1981.

[WAN 88] WANG T.T., HERBORT J.M., GLASS A.M., *The Applications of Ferroelectric Polymers*, Chapman & Hall, New York, 1988.