

Inverse Piezoelectric Effect in Polymers

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Synopsis

The condition for the inverse piezoelectric effect in polymers is discussed and a thermodynamic criteria is derived. The resulting expression is related to the electrical configuration of the polymer and several promising structures are proposed. A dynamical model of the piezoelectric effect is given, and expressions are derived for the compliance and electromechanical losses.

It is well known that certain inorganic crystals exhibit dimensional charges on application of an electrical field. This inverse piezoelectric effect has been extensively discussed in the instance of inorganic materials; however, the corresponding effect in polymeric materials has received little attention. It is the purpose of this communication to establish the basic requirements for the inverse piezoelectric effect and to propose some polymeric materials capable of satisfying these requirements. In addition a simple molecular model is proposed, and the dynamical characteristics of this model are explored.

Condition for the Inverse Piezoelectric Effect

We will first establish a general condition for the inverse piezoelectric effect. Our objective is to relate the effect to the structural characteristics of the polymer. We consider a solid in the presence of an applied stress σ and an electrical field E . Representing the dimension of the solid in the direction of σ by l and the polarization by P , the free energy change, under conditions of constant temperature and pressure, is given by the well-known result

$$dF = -ld\sigma - P dE \quad (1)$$

The cross differentiation identity gives

$$\left(\frac{\partial l}{\partial E}\right)_{T,P,\sigma} = \left(\frac{\partial P}{\partial \sigma}\right)_{T,P,E} \quad (2)$$

This result relates the inverse piezoelectric coefficient, on the left, to the change in polarization with applied stress. The latter can be expressed in a more useful way for our present purposes. Let r_i be the position vector of a charge q_i with reference to an arbitrary origin. The polarization can be expressed as¹

$$P = \sum_i q_i r_i \quad (3)$$

where the sum is taken over the charges in a unit volume. In the following we shall always assume an equal number of positive and negative charges. On introducing the position vectors for the centers of positive r_p and negative r_n charge, the polarization may be written as

$$P = (r_p - r_n) Q \quad (4)$$

where Q is the sum of the positive charges and

$$r_k = \sum q_i r_i / Q \quad (5)$$

$$r_n = -\sum q_i r_i / Q \quad (6)$$

In expression (5) it is understood that the sum is taken over the positive charges, and the sum is over the negative charges in eq. (6). The desired result follows on introducing eq. (4) into eq. (2) and using Hooke's law:

$$\left. \frac{\partial l}{\partial E} \right)_{T,P,\sigma} = \frac{Q}{Y} \frac{\partial (r_p - r_n)}{\partial \epsilon} = \frac{Q}{Y} \frac{\partial d}{\partial \epsilon} \Big|_{T,P,E} \quad (7)$$

In eq. (7) Y is Young's modulus, ϵ the strain, that is, the elongation per unit length, and d the distance vector between the centers of positive and negative charge.

It is evident from eq. (7) that the essential condition for the inverse piezoelectric effect is that a net displacement of the positive and negative centers of charge occurs when the material is subject to a strain. Thus it is required that an elongation in the direction of the applied stress must produce an electrical asymmetry in the solid. A number of polyampholytes possess this property, as is illustrated in Figure 1. The expressions for the molecular dipole moment d_m is also given, where N is the number charges of a given sign per molecule and the dimensions, a and l , are defined as shown. Application of a stress results in an increase in the length of the molecule and hence in the dipole moment. For an oriented system of dipoles this must also result in an increase in the polarization since the latter is defined as the dipole moment per unit volume. In the case of the linear structure shown in Figure 1a, no inverse piezoelectric effect is to be expected, at least in directions parallel to the long axis. We also note that the charge configuration shown in Figure 1c should result in a more pronounced effect than that shown in Figure 1b. Actually, the charge distribution shown in Figure 1c is energetically unfavorable for the linear configuration shown, and the chain would tend to fold into the more energetically favorable configuration indicated in Figure 1d.

A second class of polyampholytes with the required electrical asymmetry are the so-called "snake-cage" polyelectrolytes.² These consist of a crosslinked matrix of one polyion in which is interspersed a polycounterion. The two polyelectrolytes can electrically neutralize one another so that small mobile counterions are not necessary. In structures permitting

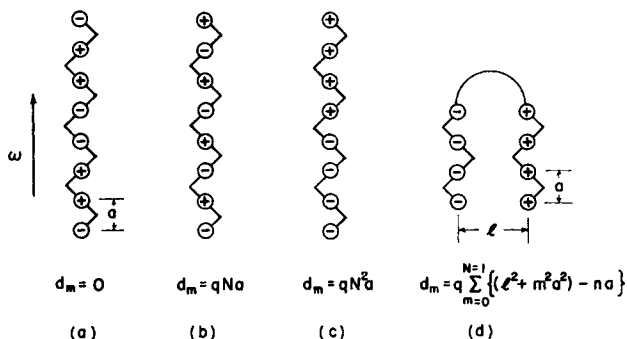


Fig. 1. The dipole moment associated with various charge configurations.

the relative motion of the polyions, polarization may occur in the presence of an electrical field together with displacement of the charge centers.

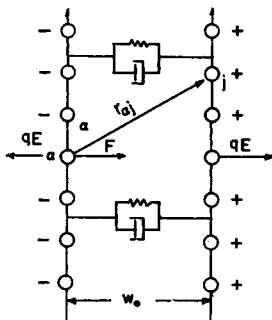


Fig. 2. Forces acting on polyampholyte molecule.

Dynamical Behavior In An Electrical Field

A simple model of the behavior of a polyampholyte in an alternating electrical field will be developed here. In order to be specific we shall consider a polyelectrolyte of the kind shown in Figure 1c consisting of anionic and cationic segments, each segment bearing N univalent fixed charges of magnitude q . In the general case the fixed charges will be surrounded by counterions which form an atmosphere of Debye length k^{-1} in a medium of dielectric constant D . In what follows we consider the electrical interaction of a single polyanion-polycation pair. However, the influence of other polymer molecules is taken into account by means of a molecular viscosity and elasticity (spring) coefficient designated by N_m and Y_m , respectively. The latter also takes into account the restoring tendency due to crosslinkages. Consider an arbitrary fixed anion designated by α in Figure 2. Assuming the usual Debye-Hückel approximation, the potential at α due to the fixed cations

$$\phi = \frac{q}{D} \sum_j \frac{\exp\{-kr_{\alpha j}\}}{r_{\alpha j}} \tag{8}$$

In the above the sum is taken over all of the anions, and $r_{\alpha j}$ is the distance between anion α and the j th cation. The total electrostatic force in the direction perpendicular to the two chains is given by $F = -\nabla\phi$, i.e.;

$$F = \frac{q^2}{D} \sum_{j,\alpha} \frac{\exp\{-kr_{\alpha j}\}}{r_{\alpha j}^2} (kr_{\alpha j} + 1) \frac{w_0}{r_{\alpha j}} \quad (9)$$

where w_0 is the equilibrium distance between the chains. This model assumes rigid polyelectrolyte chains, an assumption which seems justified because of the mutual electrostatic repulsions between like ions. On representing the displacement from the equilibrium position, w_0 , by the variable x (so that $w = w_0 + x$), the applied field by $E(t)$, the effective mass of each chain by M , and the total charge on each chain by Q , the equation of motion is

$$M\ddot{x} = QE(t) - N_m\dot{x} - Y_mx - F(w) + R(w) \quad (10)$$

Here $R(w)$ is a short-range repulsive force which will be approximated by a step function which vanishes at $w > w_0$ and becomes infinite at $w < w_0$. This repulsive force depends in part on the sorbed solvent molecules which form an incompressible shell about each polymer chain.

In order to solve the equation of motion it is necessary to linearize the expression by expanding F in a Taylor series about w_0 and to retain only the linear term. The resulting expression is then valid for only small displacements from w_0 . To this approximation we have

$$F(w) = F(w_0) + \left. \frac{\partial F}{\partial w} \right|_0 x \quad (11)$$

where the derivative is evaluated at w_0 . The equation of motion now may be written for the region $w > w_0$ as

$$M\ddot{x} + N_m\dot{x} + \left[Y_m + \left. \frac{\partial F}{\partial w} \right|_0 \right] x = QE(t) - F(w_0) \quad (12)$$

It is evident that the condition $w > w_0$ implies that a net extensive force is acting on the polymer tending to increase w so that we must have

$$E(t) > F(w_0)/Q = E_m \quad (13)$$

This last expression together with eq. (9) determines, in principle, the minimum field E_m required for the inverse piezoelectric effect. One difficulty with this type of calculation is that of estimating w_0 , the average equilibrium distance between the polymer molecules. This problem has been discussed by Katchalsky and Lifson³ as well as by Rice and Harris.^{4,5} For the present purposes it is sufficient to note that E_m will decrease with increasing ionic strength, dielectric constant, and degree of sorption of solvent.

Turning to the solution of eq. (12) we assume that the applied field

consists of steady-state component upon which is superimposed a small alternating component of frequency ω and magnitude E_0 , i.e.,

$$E(t) = E_m + E_0 (1 + e^{j\omega t}) \quad (14)$$

It is evident that this applied field satisfies eq. (13). With this applied field the solution to eq. (12) is (for the initial conditions $x = \dot{x} = 0$ at $t = 0$)

$$x = \frac{e^{-\alpha t}}{\beta} \left\{ [E\omega K j - E_0 \left(\frac{1}{\gamma} + K \right) (-\alpha + \beta)] e^{-\beta t} - [E\omega K j + E_0 \left(\frac{1}{\gamma} + K \right) (\alpha + \beta)] e^{\beta t} \right\} + E_0 \left[\frac{1}{\gamma} + K e^{j\omega t} \right] \quad (15)$$

where

$$\alpha = N_m/2M$$

$$\beta = [(N_m/2M)^2 - (\gamma/M)]^{1/2}$$

$$\gamma = Y_m + \left(\frac{\partial F}{\partial w} \right)_0$$

$$K = 1/[(\gamma - M\omega^2) + j\omega N_m]$$

Solution (15) holds provided $\beta \neq 0$. When the latter is the case the solution may also be readily obtained but it will not be required here.

Discussion

Certain features of the above solution are worthy of comment. The electrostatic factor $(\partial F/\partial w)_0$ serves to modify the spring constant Y_m so that the significant quantity is now γ defined above. The transient portion of the solution decays in an oscillatory manner when $\gamma/M > \alpha^2$ and exponentially when $\gamma/M < \alpha^2$. It must also be noted that an instability occurs when $\gamma = 0$ so that

$$-\left(\frac{\partial F}{\partial w} \right)_0 = Y_m \quad (16)$$

Physically this condition corresponds to the situation where E_m just exceeds the electrostatic and elastic counterforce. As a result, x will tend to increase indefinitely until checked by factors external to the present formulation.

The steady-state solution may be expressed somewhat differently by writing the compliance $K(\omega)$, as

$$K(\omega) = [(1 - j\omega\tau)/(1 + \omega^2\tau^2)](\tau/N_m) \quad (17)$$

where

$$\tau = N_m/(\gamma - M\omega^2) = N_m/[M(\omega_0^2 - \omega^2)] \quad (18)$$

The frequency ω_0 is the resonant frequency for a hypothetical polymer with zero viscosity. On introducing the above notation, the steady-state solution becomes

$$x = E_0[K(0) + K(\omega)e^{j\omega t}] \quad (19)$$

The viscoelastic properties of the system may now be calculated as usual. Thus the energy loss W per cycle is

$$W = E_0^2 \pi \omega \tau^2 / [N_m(1 + \omega^2 \tau^2)] \quad (20)$$

This loss has a maximum at

$$\omega = 1/\tau^2$$

Similarly the loss per second is

$$W = E_0^2 \omega^2 \tau^2 / [2N_m(1 + \omega^2 \tau^2)] \quad (21)$$

We see from eq. (21) that there is no loss when $\omega = 0$. However, in the case of polyelectrolytes with small mobile counterions, additional losses will occur due to d.c. conductivity and are given by the well-known expression $I^2 R$, where I is the d.c. current and R is the electrical resistance of the media. This loss will not be significant in systems in which ions of both signs are large polyelectrolytes.

Small ions will alter the charge on the polymer in the presence of weakly ionizing groups or when complex formation occurs. This effect was also neglected in the above treatment, though with a little additional algebraic complexity it could readily be taken into account.

Finally, some problems inherent in the practical realization of the inverse piezoelectric effect will be briefly considered here. As indicated above, the effect is to be expected in molecularly oriented crystals. In the case of more or less randomly oriented specimens the response to the applied field would tend to be statistically cancelled out. However, in the latter case a significant effect may be observed, provided that the molecules are capable of orienting themselves in the applied field. A more detailed discussion of the actual response of polymers in applied fields will be given in a subsequent communication.

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Résumé

La condition pour obtenir l'effet piézoélectrique inverse dans les polymères est discutée et on en déduit un critère thermodynamique. L'expression résultante est reliée à la configuration électrique du polymère et plusieurs structures plausibles sont proposées. Un modèle dynamique de l'effet piézoélectrique est donné et on déduit des expressions pour les pertes électromécaniques.

Zusammenfassung

Die Bedingung für den inversen piezoelektrischen Effekt bei Polymeren wird diskutiert und ein thermodynamisches Kriterium abgeleitet. Der abgeleitete Ausdruck wird zu der elektrischen Konfiguration des Polymeren in Beziehung gesetzt und verschiedene mögliche Strukturen vorgeschlagen. Ein dynamisches Modell für den piezoelektrischen Effekt wird angegeben und Ausdrücke für die Nachgiebigkeit und die elektromechanischen Verluste werden abgeleitet.

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