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INVERSE PIEZOELECTRIC EFFECT
IN POLYMERS

by

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SUMMARY

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.

Inverse Piezoelectric Effect in Polymers

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It is well known that certain inorganic crystals exhibit dimensional changes 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 is 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

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

The cross differentiation identity gives

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

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 as (1)

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

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

$$r_k = \frac{\sum q_i r_i}{Q} \quad (5)$$

$$r_n = -\frac{\sum q_i r_i}{Q} \quad (6)$$

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

$$\left. \frac{\partial f}{\partial E} \right)_{T,p} = \frac{Q}{Y} \frac{\partial (r_p - r_n)}{\partial \epsilon} = \frac{Q}{Y} \left. \frac{\partial d}{\partial \epsilon} \right)_{T,p,E} \quad (7)$$

In (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 (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 passes 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 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 1c should result in a more pronounced effect than that shown in 1b. Actually the charge distribution shown in 1c is energetically unfavorable for the linear configuration shown and the chain would tend to fold into the more energetically favorable configuration indicated in 1d.

A second class of polyampholytes with the required electrical asymmetry are the so-called "snake-cage polyelectrolytes" (2). These consist of a cross linked matrix of one poly-ion in which is interspersed a poly-counter ion. The two polyelectrolytes can electrically neutralize one another so that small mobile counter ions are not necessary. In structures permitting the relative motion of the poly-ions, polarization may occur in the presence of an electrical field together with displacement of the charge centers.

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 counter ions 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-Huckel approximation, the potential at α due to the fixed cations

$$\phi = \frac{q}{D} \sum_j \frac{e^{-kr_{\alpha j}}}{r_{\alpha j}} \quad (8)$$

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.;

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

where w_0 is the equilibrium distance between the chains. This model assumes rigid polyelectrolytes chains; an assumption which seems justified because of the mutual electrostatic repulsions between like ions. 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

$$M\ddot{x} = Q \bar{E}(t) - N_m \dot{x} - Y_m x - F(w) + R(w) \quad (10)$$

Here $R(w)$ is a short range repulsive force which will be approximated by a step function which vanishes at for $w > w_0$ 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

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

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

$$E(t) > \frac{F(w_0)}{Q} \equiv E_m \quad (13)$$

This last expression together with (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 Lifson (3) as well as by Rice and Harris (4). 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 (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 (13). With this applied field the solution to (12) is (for the initial conditions $x = \dot{x} = 0$ at $t = 0$)

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

where

$$\alpha = \frac{N}{2M} m$$

$$\beta = \left[\frac{N_m^2}{2M} - \frac{\gamma}{M} \right]^{1/2}$$

$$\gamma = Y_m + \left. \frac{\partial F}{\partial w} \right|_0$$

$$K = \frac{1}{(\gamma - M\omega^2) + j\omega N_m}$$

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 $\left(\frac{F}{w} \right)_0$ serves to modify the spring constant Y_m so that the significant quantity is now 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 $\alpha = 0$ 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 counter-force. 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

$$K(\omega) = \frac{1 - j\omega\tau}{1 + \omega^2\tau^2} \frac{\gamma}{N_m} \quad (17)$$

where

$$\tau = \frac{N_m}{\gamma - M\omega^2} = \frac{N_m}{M(\omega_o^2 - \omega^2)} \quad (18)$$

The frequency ω_o is the resonant frequency for a hypothetical polymer with zero viscosity. Introducing the above notation the steady state solution becomes

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

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

$$W = \frac{E_o^2 \pi \omega \tau^2}{N_m (1 + \omega^2 \tau^2)} \quad (20)$$

This loss has a maximum at

$$\omega = \frac{1}{\tau^2}$$

Similarly the loss per second is

$$W = \frac{E_o^2 \omega^2 \tau^2}{2 N_m (1 + \omega^2 \tau^2)} \quad (21)$$

We see from equation (21) that there is no loss when $\omega = 0$.

However, in the case of polyelectrolytes with small mobile counter ions additional losses will occur due to dc conductivity and are given by the well known expression I^2R where I is the dc current and R 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.

References

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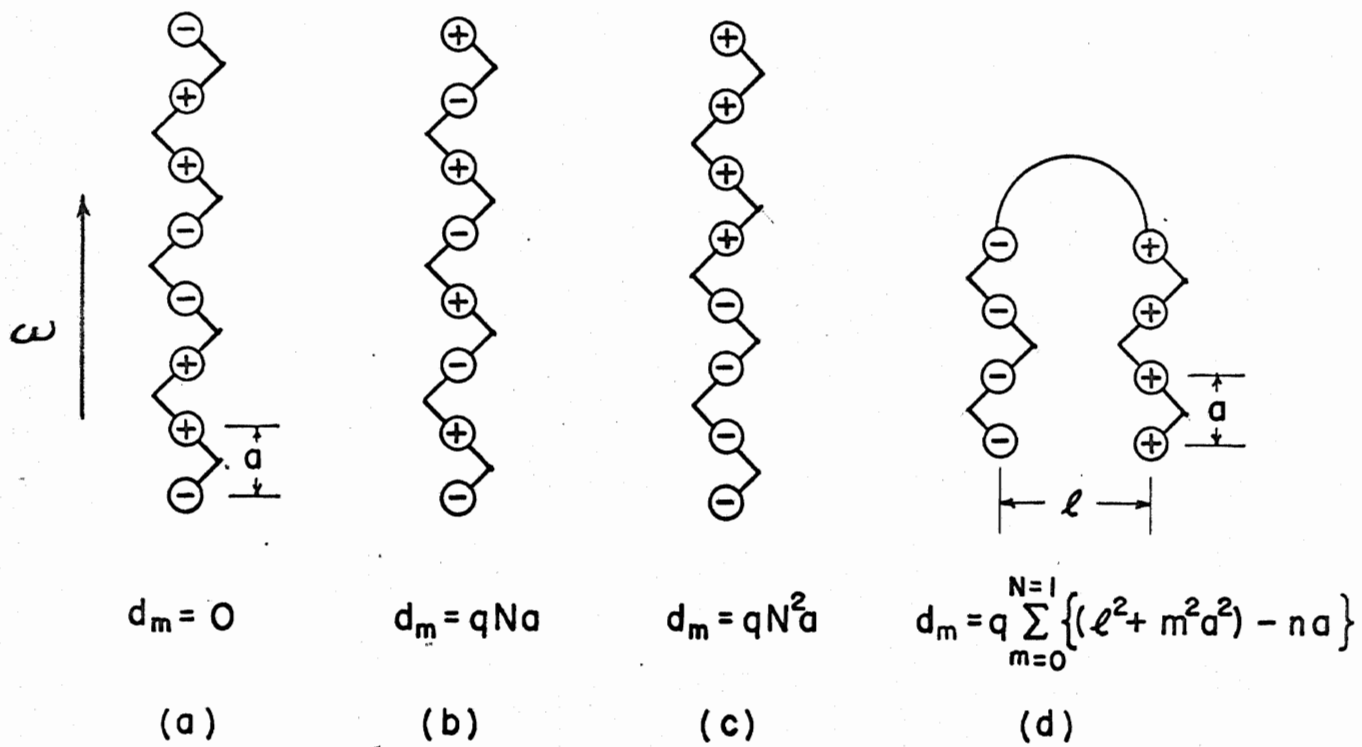


Figure 1

The dipole moment associated with various charge configurations.

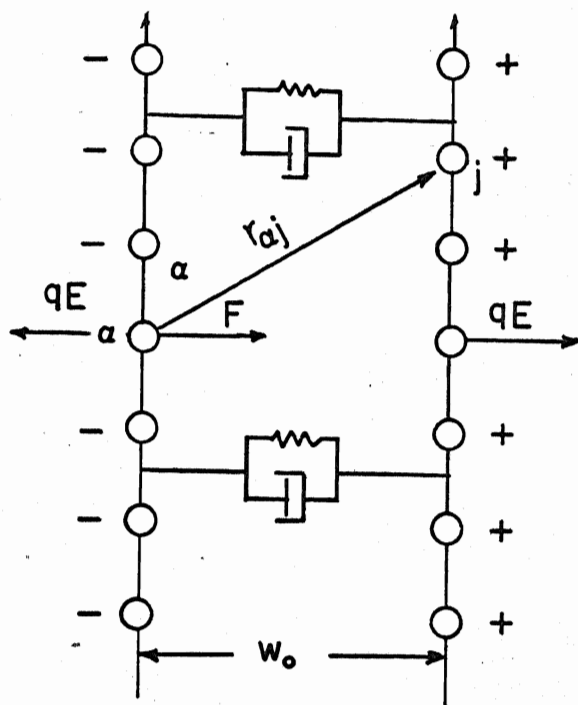


Figure 2

Forces Acting On Polyampholyte Molecule