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The Electret Effect in Polymers. Advances in the Preparation and Application of Electrets

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Recent advances in the development of the theory of electret effects in polymers (except photo- and bio-electrets) are discussed: they include the phenomenological theory, the nature of the residual polarisation and of the injected charge, and the nature of the piezo- and pyro-effects in polymer electrets. Successful applications of electret-thermal analysis to the study of molecular mobility in polymers are discussed. The principal directions of the practical exploitation of polymer electrets are outlined. The goals of further studies and of technological developments are defined. 99 references.

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I. INTRODUCTION

The term electret effect describes the ability of dielectrics to develop electric charges and retain them for long times. Polymer electrets can be prepared by various methods: by cooling the polymer in an electric field (thermo-electrets), by polymerisation or cross-linking in an electric field (chemo-electrets), by the application of a strong electric field (electro-electrets), by charging in a corona discharge (corona electrets), by exposure to radiation (e.g. to an electron beam, radiation electrets), and by evaporating a solution of the polymer in an electric field (cryo-electrets). Electrets have been obtained also by mechanical deformation (mechano-electrets), by frictional electrification (tribo-electrets), and by exposing a polymer to a magnetic field (magneto-electrets).[1]

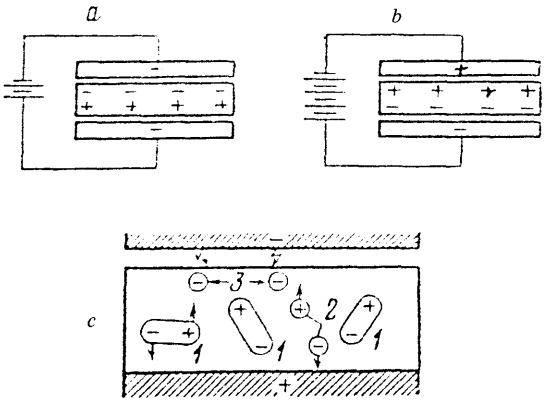


Figure 1. Configuration of charge and electrodes in an electret: (*a*) hetero-charged electret, (*b*) homo-charged electret, (*c*) charges in the electret (*1*, oriented dipole, and dipoles undergoing orientation; *2*, displaced ions; *3*, injected charge carriers).

Electrets can be classified according to the type of charge into those whose charge is due to the orientation of dipoles and the displacement of ions "frozen" in the electric field, and which therefore retain a residual polarisation P or "hetero-charge", and the electrets whose charge is due to carriers injected from outside ("homo-charge", or real free charge σ_p, see Fig.1). In a real electret the surface charge density σ_{eff} is equal to the sum of these two types of charge (of opposite sign):

$$\sigma_{eff} = \sigma_p - P \cdot,$$

If residual polarisation is initially absent ($P = 0$), some polarisation will appear during storage under the influence of the internal field of the electret. The changes in surface charge density are determined by the time dependence of σ_p and P.

II. FORMATION AND STABILITY OF ELECTRET CHARGES

1. Phenomenological Theory

The phenomenological theory of electrets gives a general description of the electret effect. By formulating various hypotheses on the role of the charges σ_p and P different expressions can be obtained for the time dependence $\sigma_{eff}(t)$. A detailed phenomenological theory was developed by Gubkin[2], who also discussed alternative phenomenological theories.

According to modern views, electrets contain a residual, frozen polarisation P and a real charge σ_p. It is usually assumed that the polarisation decays by an exponential law with a relaxation time τ_p, and that the real charge also decreases exponentially and is determined by the Maxwell relaxation time τ_M:

$$\begin{gathered} P(t) = P_0 \exp(-t/\tau_p) \\ \sigma_p(t) = \sigma_p(0) \exp(-t/\tau_M) \\ \tau_M = \varepsilon_0 \varepsilon \rho \ . \end{gathered} \qquad (1)$$

In these expressions P_0 and $\sigma_p(0)$ are the initial values of P and σ_p, ρ is the (volume) electrical resistivity, ε is the dielectric constant, and ε_0 is the permittivity of free space 8.854×10^{-12} F m^{-1}. If electrodes are placed near the electret, and a gap l is left between the electret surface and the electrodes, the parameter ε in Eqn.(1) is replaced by the coefficient K, defined as

$$K = \varepsilon + L/l$$

where L is the thickness of the electret[2]. The result is an expression in the form of

$$\frac{d\sigma_{eff}(t)}{dt} + \frac{\sigma_{eff}(t)}{\varepsilon_0 K\rho} + \frac{dP(t)}{dt} = 0 .$$

In the theory developed by Perlman[3] no allowance is made for the formation of residual polarisation during the preparation of the electret: a "ready-made" electro-electret is assumed, and only the changes in polarisation due to ageing are discussed. Other workers used slightly different initial assumptions[4,5], but they all obtained expressions of the type of

$$\sigma_{eff}(t) = \sum_i \sigma_i(0) \exp(-t/\tau_i)$$

where in most cases $i = 1, 2, 3$.

Let us consider the case of the thermo-electret. The expression for the polarisation induced by the internal field of the electret during ageing is

$$P = \varepsilon_0 \int_0^t E(t') \frac{d\chi(t-t')}{dt'} dt$$

where E is the intensity of the internal field of the electret, χ is the dielectric susceptibility, consisting of the susceptibility corresponding to polarisation, $\chi_\infty = (\varepsilon - 1)$, established instantaneously and constant in time, and the time-dependent susceptibility $\chi_p(t)$, associated with the polarisation slowly induced under the influence of the internal field:

$$P = P_{max}(1 - e^{-t/\tau_p})$$

where $P_{max} = P_0 = \varepsilon_0 \Delta\varepsilon E$ (and $\Delta\varepsilon$ is the increment of the dielectric constant, see below). The general time dependence $\sigma_{eff}(t)$ in this case becomes

$$\sigma_{eff}(t) = \sigma_p(0) e^{-t/\tau_M} - P_0 e^{-t/\tau_p} - \frac{1}{\varepsilon\varepsilon_0} \int_0^t \sigma_{eff}(t) \frac{d[\chi(t-t')]}{dt'} dt .$$

By solving this equation (using the Laplace transform) we obtain the following expression for an open-circuited electret

$$\sigma_{eff}(t) = \frac{\sigma_p(0)[(1/\tau_p) - (1/\tau_M)]}{[(1/\tau) - (1/\tau_M)]} e^{-t/\tau_M} + \left[\frac{\sigma_p(0)(\Delta\varepsilon/\varepsilon\tau_p)}{(1/\tau) - (1/\tau_M)} - P_0\right] e^{-t/\tau} \quad (2)$$

where $\tau = \tau_p \varepsilon/(\varepsilon + \Delta\varepsilon)$. Putting $\varepsilon = \varepsilon_\infty$ and $\Delta\varepsilon + \varepsilon_\infty = \varepsilon_{st}$ we obtain $\tau = \tau_p \varepsilon_\infty / \varepsilon_{st}$, i.e. an expression for the decay time constant of the charge, where τ_p is the rise time constant of the charge in the same condenser[6].

In real electrets τ_p is often much smaller than τ_M: in this case Eqn.(2) simplifies to

$$\sigma_{eff}(t) = \frac{\varepsilon\sigma_p(0)}{\varepsilon + \Delta\varepsilon} e^{-t/\tau_M} + \left[\sigma_p(0)\frac{\Delta\varepsilon}{\varepsilon + \Delta\varepsilon} - P_0\right] e^{-t/\tau} . \quad (3)$$

or

$$\sigma_{eff}(t) = \frac{\varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) e^{-t/\tau_M} + \left[\frac{\varepsilon_{ст} - \varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) - P_0\right] e^{-t/\tau} . \quad (4)$$

In the presence of a gap between the electrode and the electret we replace ε by K in Eqns.(3) and (4).

In practice the real charge is often found to have two components: a rapidly decaying (σ'_p) and a slowly decaying (σ_p) component. Assuming that the decay time constant of σ'_p is so small that slow polarisation cannot develop in the field of this charge we obtain

$$\sigma_{eff}(t) = \sigma'_p(0) e^{-t/\tau'_M} + \frac{\varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) e^{-t/\tau_M} + \left[\frac{\varepsilon_{st} - \varepsilon_\infty}{\varepsilon_{st}} \sigma_p(0) - P_0\right] e^{-t/\tau} . \quad (5)$$

Each term in Eqn.(5) has a clear physical significance. The first describes the capture of injected carriers by shallow traps near the surface of the dielectric. The σ'_p component of the charge plays an important role in static electrification and in charging in a corona discharge[7]: this charge can easily be removed by wrapping the electret in a metal foil or by applying an earthed electrode to it.

The second term depends on the capture of injected carriers by deep traps, whose energy is relatively high (see below). Thus the charge component σ_p can relax (at least partially) through compensation by the charge carriers of the polymer itself, and therefore the activation energy for the relaxation of this charge component at temperatures above the glass transition point is equal to the temperature coefficient of the conductivity of the polymer[8].

The third term in (5) is determined by polarisation. A thermo-electret prepared from a polar polymer will have a residual polarisation P_0. Since in many cases $\tau < \tau_M$ the presence of P_0 shortens the time needed to stabilise the electret. From the plots (Fig.2) of the $\sigma_{eff}(t)$ dependence for an electret charged in a corona discharge and for a thermo-electret we note that the latter stabilises relatively quickly whereas the former needs a long time to reach a quasi-constant value of σ_{eff}. [Stability is defined as a state in which σ_{eff} remains within a prescribed range (±15%, say) of its nominal value throughout the useful life of the electret (10 years, say).] Stabilisation can be accelerated by corona charging at elevated temperatures or by heating the already charged electret. In this case τ decreases, and a quasi-constant value of σ_{eff} is established more rapidly. For a polymer with a small value of the difference $\varepsilon_{st} - \varepsilon_\infty$ (i.e. a non-polar polymer), or a polymer with $\tau \geq \tau_M$ (a polar polymer with a very high glass transition temperature, such as a polycarbonate with a norbornane ring[9]) the stabilisation time is reduced to the very short time needed for the decay of the σ'_p component. We note that a good example of a non-polar polymer suitable for the preparation of stable electrets is a film of polytetrafluoroethylene or of the copolymer of tetrafluoroethylene and hexafluoropropene.

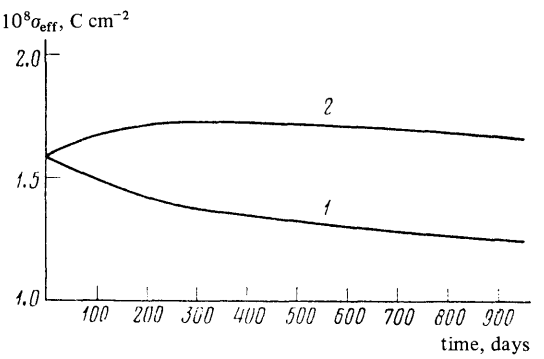


Figure 2. Time dependence of the surface charge σ_{eff} of electrets made from a polar polymer (polycarbonate): *1*) corona electret, *2*) thermo-electret ($\rho_{res} = 1.3 \times 10^{21}$ Ohm cm, $\varepsilon = 3$, $\Delta\varepsilon = 0.44$, $\tau = 8 \times 10^6$ s).

The constancy of P is determined by the molecular mobility, whereas the stability of the charge σ_p is determined by the electrical conductivity (which is also largely dependent, however, on the molecular mobility).

Polarisation can arise also in the crystalline regions of polar polymers. Thus, a rearrangement of the crystalline structure can be induced in poly(vinylidene fluoride) and polyamide-11 by strong electric fields [over 10^8 V m^{-1} in the case

of poly(vinylidene fluoride)]. Rotation of the $-CH_2-CF_2-$ chain in the direction of the field is energetically favourable, and results in a change of the crystal structure from the low-polarity α form to the more polar, spontaneously polarisable β form, in which P_0 can be as high as 0.1 C m^{-2}.[10]

2. Residual Polarisation

Let us consider the development of residual polarisation[11]. We shall heat the dielectric to the polarisation temperature T_p, which is higher than the transition temperature (for example, the glass transition temperature T_g, see Fig. 3). At temperature T_p the dielectric constant rises as a result of the increased segmental mobility which allows the dipoles to become oriented in the field. When the electric field E_p is applied the polarisation of the sample is described by the equation

$$P(T_p) = \varepsilon_0[\varepsilon(T_p) - 1] \cdot E_p \ .$$

If the dielectric is now cooled in the field to the temperature T_K, where $T_K < T_g$, and the external field is removed, the polarisation of the sample decreases by the amount

$$P(T_K) = \varepsilon_0[\varepsilon(T_K) - 1]E_p \ .$$

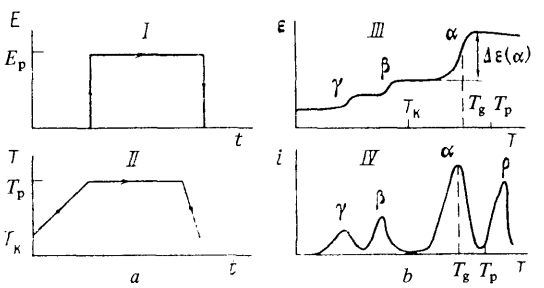


Figure 3. Preparation of a thermo-electret. (*a*) time dependences: *I*) field strength E_p, *II*) temperature *T*; (*b*) temperature dependences: *III*) dielectric constant, *IV*) TSD current during heating of the thermo-electret.

Since $\varepsilon(T_p)$ is greater than $\varepsilon(T_K)$, $P(T_p)$ is greater than $P(T_K)$, and the difference between these quantities is equal to the residual polarisation:

$$P_0 = P(T_p) - P(T_K) = \varepsilon_0[\varepsilon(T_p) - \varepsilon(T_K)]E_p \qquad (6)$$

or

$$P_0 = \varepsilon_0 \Delta\varepsilon E_p \ .$$

Here $\Delta\varepsilon$ is the temperature increment of the dielectric constant, approximately equal to the frequency increment of the dielectric constant at the transition temperature T_g: $\Delta\varepsilon \cong \varepsilon_{st} - \varepsilon_\infty$ (where ε_{st} is the static dielectric constant, and ε_∞ is the dielectric constant for a field of infinite frequency). Thus we have

$$P_0 = \varepsilon_0(\varepsilon_{st} - \varepsilon_\infty)E_p \ . \qquad (7)$$

The equality of P_0 [calculated by formula (6)] and of the heterocharge was established experimentally for polycarbonate and poly(methyl methacrylate) thermo-electrets polarised at $E_p < 10^6$ V m^{-1}, for which the injection of charge carriers is small. The values of $P(T_p)$ and $P(T_K)$ can be determined experimentally by integrating the charging currents at T_p and the discharge currents at T_K (after subtracting the conduction currents):

$$P(T_p) = \int_0^\infty i_p(T_p)\,dt; \quad P(T_K) = \int_0^\infty i_p(T_K)\,dt$$

where i_p is the current density.

However, the relationship (7) is not obeyed if we use the frequency increment of the dielectric constant obtained from the frequency dependence of ε′ and ε″ at temperatures higher than T_g.

It has been reported[12] that in polar polymers such as poly(vinyl chloride) the dielectric constant in the glass transition region increases as the measurement frequency is decreased to 0.1, 0.01, and 0.001 Hz, and the effect was ascribed to the increase in the effective dipole moment μ_{eff} caused by the increase in length of the segment (the mobile portion of the chain). Since $\Delta\varepsilon$ is proportional to $N\mu_{eff}^2$,

$$\Delta\varepsilon \simeq \text{const} \cdot N\mu_{eff}^2/T$$

an increase in the length of the segment (by a factor of 2, say) lowers the concentration *N* of dipoles by the same factor, but it raises μ_{eff}^2 by a factor of 4 (the parameter μ_{eff} contains contributions from all the groups present in the segment: $\mu_{eff} \cong n\mu_0$). The steep increase of ε near T_g is treated[12] as a typical ferroelectric effect, and T_g is identified with the Curie temperature of poly(vinyl chloride).

Thus Eqn. (7) is valid only if the measurement of ε is carried out under the conditions used in the preparation of the electret (frequency range, polarisation and depolarisation time, field strength). The dielectric losses ε″ and the dielectric constant ε′ can be calculated from the charging and discharging currents by using the Fourier transform

$$\varepsilon'' = \frac{1}{C_0 V}\int_0^\infty i_p \sin\omega t \cdot dt$$

$$\varepsilon' = \frac{1}{C_0 V}\int_0^\infty i_p \cos\omega t \cdot dt \ .$$

For ε″ we have the simplified formula[13]

$$\varepsilon'' = i_n/2\pi f_{equiv} C_0 V \ .$$

The equivalent frequency of the measurements is given by the expression

$$f_{equiv} = 0{,}1/t_p \ . \qquad (8)$$

Since the polarisation time t_p is tens of minutes, $f_{equiv} \cong 10^{-2}$–10^{-4} Hz. Since electrets are stored for many months or years, the parameters ε and $\Delta\varepsilon$ which appear in expressions (2)–(5) should be determined at $f_{equiv} \cong 10^{-6}$–10^{-9} Hz.

3. Charge Injection

The application of a strong electric field to a polymer causes injection of charge carriers into the polymer. The stability of this charge (σ_p) is formally determined by the electrical conductivity $\gamma = 1/\rho$. There are two different theories of the nature of electrical conduction in polymers. According to the first the electrical conductivity of polymers is ionic and depends on the concentration of impurities[14]. According to the second it is of the electron–hole type[15]. Ionic conduction is predominant at temperatures above T_g, when the segmental mobility is high, and also in plasticised polymers, for example of the poly(vinyl chloride) type.

Electronic charge transfer processes are predominant at high field strengths (above 10^6 V m^{-1}) in polymers at temperatures below T_g, in polymers with conjugated bonds (semiconducting polymers), and in polymer dielectrics with a relatively large number of conjugated bonds (for example, poly-imides[16]). However, even at low temperatures (below T_g) the contact charging of a dielectric without an applied external field on a clean surface in a vacuum takes place by electron transfer[17], whereas in air the charging is determined by the migration of ions in the adsorption layers on the surface[18].

The injected charge σ_p is produced by the injection of electrons and holes from the electrodes[19] (electro- and thermo-electrets), the injection of electrons, holes, and (or) ions from the air (corona electrets, electro- and thermo-electrets with a poor electrode–electret contact), the injection of electrons, holes, and ions from a liquid (in the case of charging from liquid electrodes), and by electron injection when the sample is irradiated with a beam of electrons. During charging in a corona discharge the main process consists in sorption of ionised air molecules on the polymer surface followed by electron transfer (from the molecule to the surface) and desorption of the molecules. At normal field strengths the charge carriers penetrate to a small depth into the polymer dielectric (1–1.5 μm), forming a charged layer ("cloud") which slowly diffuses into the dielectric[20]. The surface layer of dielectric with its high concentration of injected carriers has an abnormally high electrical conductivity. Depending on the "short-circuiting" conditions of the electret (i.e. on the disposition of the electrodes) the charge carriers will diffuse under the influence of the field of the electret either into the bulk of the sample or towards the nearest surface. When the electret is stored some of the carriers in shallow traps are captured by the deep traps. The depth of these traps determines the stability of the charge σ_p. The retrapping of the charge carriers can be accelerated by heating the electret.

The nature of the deep traps, which determines the value and the stability of σ_p, is discussed in Ref. 21. The injected charge carriers interact with the polymer molecules. For example, the interaction of electrons with a fluorinated polyolefin chain (polytetrafluoro-ethylene, tetrafluoro-ethylene–hexafluoro-propene copolymer) produces stable ions because of the high electron affinity of the fluorine molecule. The electrons can also interact with the carbonyl group to give charged groups of the $CH_2–CO^-–CH_2–$ type[22].

Impurity ions and phase separation boundaries can also act as traps. Electrons near an amorphous–crystalline interface of the polymer are slowed down, and their field induces the reorientation of neighbouring dipoles and polar groups. If the adjacent units of the molecular chain have sufficient mobility, the conformation of the chain can change. For example, in poly(ethylene terephthalate), studied by frustrated total internal reflection i.r. spectroscopy, charging in a corona discharge produces a change in the conformation of the chains in the surface layer: the *trans* conformation is partially converted into the *gauche* conformation according to the observed changes in the i.r. spectral absorption bands at 502, 633, 897, 973, and 1172 cm^{-1}. When the electret is discharged the original conformation is partially restored[23].

Studies of the thermally stimulated depolarisation currents of electrets containing injected charges have shown that the TSD maxima for the discharge of injected homo-charge (ρ maxima) occur at the same temperatures as the maxima of the molecular mobility at the crystallite boundaries (α_c relaxation). We should stress that this type of molecular mobility can seldom be detected by the traditional methods of dielectric spectroscopy because the contributing dipoles are weak and few in number: the position of the ρ maximum on the temperature scale corresponds to the maximum of the dynamic mechanical losses at a frequency of ~10^{-4} Hz.[24] Increasing the aggregate surface area of the crystallites per unit volume of the polymer (for example, by decreasing the crystallite size while keeping the overall crystallinity constant) raises the α_c maximum, i.e. it increases the trapped charge (for example, in polychlorotrifluoroethylene).[25]

The TSD current maximum corresponding to relaxation of the injected charge is called the ρ maximum because the activation energy for the relaxation of this component of the charge is equal to the temperature coefficient of the electrical resistivity ρ. Evidently, charge relaxation is due to the mobility of the polymer ions or of the injected ions: the motion of these ions can compensate the trapped space charge.

4. Surface Density of Charges

The time for which the surface density of charge σ_{eff} persists is determined by the stability of σ_p and P. Ultimately, the determining factor is the low electrical conductivity of the electret, which is produced in polymer dielectrics by a low concentration of intrinsic, free charge carriers and also (under the normal conditions of use of the electret) by a low internal field, especially if the electret is "shorted", i.e. in the presence of closely spaced electrodes. Under these conditions the electrical conductivity of the sample falls to 10^{-23} Ohm^{-1} m^{-1} or less[26].

The maximum value of the charge σ_{eff} is limited by the dielectric strength of air[1]. It increases as the thickness of the electret decreases:

$$\sigma_{eff}^{max} = 100\,\varepsilon_0[200 + (3\varepsilon/L)^{1/2}]^2 .$$

In this expression ε is the dielectric constant of the electret. On the other hand the maximum surface potential V_{max} decreases as the thickness decreases: $V = \sigma_{eff}L/\varepsilon\varepsilon_0$. For samples 2 mm thick the maximum value of σ_{eff} is ~5×10^{-5} C m^{-2}, and for films 10 μm thick it is ~2×10^{-4} C m^{-2}.[1]

III. THE ELECTRET EFFECT IN POLYMERS

1. Electret-thermal Analysis of Polymers

The study of the kinetic relaxation characteristics of electret charges can be greater accelerated by a programmed heating of the electret with measurement of the thermally stimulated depolarisation (TSD) current.

The relaxation parameters are calculated from the TSD currents[11] by formulae which assume that 1) the electret contains only one type of dipole, 2) all the dipoles have the same relaxation time τ, and 3) the temperature dependence of the relaxation time is exponential,

$$\tau = A \exp(W/RT)$$

where R is the gas constant, A is the pre-exponential factor, and W is the activation energy (temperature coefficient) of the charge relaxation. With these assumptions we obtain the following formula for the TSD current of an electret heated at a linear rate b:[27–29]

$$i(T) = -\frac{P_0}{A}\exp\left[-\frac{W}{RT} - \frac{1}{bA}\int_{T_0}^{T}\exp\left(-\frac{W}{RT}\right)dT\right] \qquad (9)$$

where T_0 is the initial temperature. The relaxation time of the charge (τ_{max}) at the temperature of the TSD current maximum is given by the expression

$$\tau_{max} = RT_{max}^2/Wb\,. \qquad (10)$$

In the initial portion of the plot of TSD current against temperature we can use the expression

$$\lg i = \text{const} - 0{,}4343\ W/RT\,. \qquad (11)$$

By using Eqns.(9)–(11) we can calculate the macroscopic characteristics W, T_{max}, and A. However, these quantities cannot be related to the characteristics of the dielectric relaxation of the polymer obtained from measurements over a range of frequency and temperature. This is most probably because the above assumptions are never strictly applicable. Polymers often contain several types of dipole (polar groups), or if they contain dipoles of one type only their mobility can arise in two ways: either cooperatively, in a relatively long section (segment) of the macromolecule, or by being in a short side-chain (possibly in conjunction with other groups of the chain). The former alternative gives dielectric losses of the dipole segment type, the latter of the dipole group type. The second assumption (that all the dipoles have the same relaxation time) is also invalid. Polymers always show some range of dipole relaxation times, characterised by a distribution function. If the form of this function is known (for example, a Cole–Cole or a Fuoss–Kirkwood distribution) the expressions which relate the complex dielectric constant ε^* to the relaxation time become simpler, and the relationships of the components ε' and ε'' with each other and with the relaxation time are also simplified. The third assumption is exactly satisfied for dipole group relaxation and approximately satisfied for dipole segment relaxation.

These considerations suggest that the relaxation characteristics of the electret charges obtained from the TSD currents may be correlated with the characteristics normally used in dielectric spectroscopy. The charging current of a condenser in which the dielectric relaxation is described by the Cole–Cole theory is given by the formula[13]

$$i_p = \frac{Q}{\tau}\frac{1}{\Gamma(1-\alpha)}\left(\frac{t}{\tau}\right)^{1-\alpha} \text{(for } t \ll \tau)\,.$$

It follows from this expression that for a change in the temperature of the experiment (which results in a change of τ) we can write

$$i_p = \text{const}\cdot t^{-(1-\alpha)}\exp[-(1-\alpha)E/RT]\,.$$

Thus the experimental temperature coefficient W is related to the apparent activation energy of the dipole relaxation E by the expression

$$W = (1-\alpha)E \qquad (12)$$

where $(1 - \alpha)$ is a parameter which characterises the distribution of relaxation times according to the Cole–Cole theory, and is approximately equal to the distribution parameter λ of the Fuoss–Kirkwood theory[13]. By allowing for Eqn.(12) we can use formulae (9)–(11) to determine the dielectric relaxation parameters in the low frequency region if we also note that determining the relaxation characteristics from the TSD currents is equivalent to determining the dielectric losses at the frequency f_{equiv} by Eqn.(8) with $t_p = \tau_{max}$ [where τ_{max} is given by Eqn.(10)].

A more satisfactory description of the experimental results can be obtained by assuming that the parameters E and λ are independent of temperature[11]. In this case the TSD current is given by the expression

$$i(T) = -\frac{P_0 E\lambda b}{\pi RT^2}\,\text{sech}\left[\frac{E\lambda}{R}\left(\frac{1}{T}-\frac{1}{T_{max}}\right)\right] \qquad (13)$$

where T_{max} is the reference temperature, which for large values of E/RT becomes equal to the temperature of the TSD current peak.

The dielectric losses at the frequency f_{equiv} can be calculated if the TSD current is known:

$$\varepsilon''(T) = \pi RT^2 i(T)/2\varepsilon_0 E E_p b\,. \qquad (14)$$

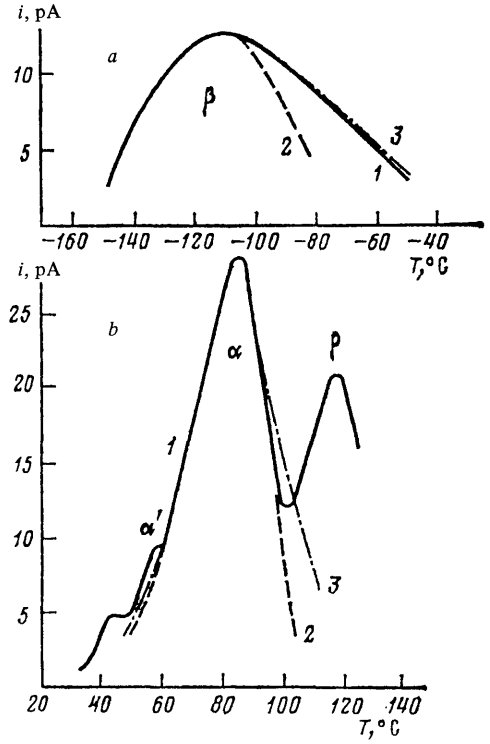


Figure 4. Temperature dependence of the TSD current of a poly(ethylene terephthalate) film thermo-electret (ETA thermogram): (*a*) low-temperature region (β relaxation); (*b*) high-temperature region (α relaxation); *1*) experimental, *2*) calculated by formula (9), *3*) calculated by formula (13).

The expressions obtained by making these assumptions [(13) and (14)] are fairly simple, but they satisfactorily describe the TSD current in the dipole group relaxation region and also, to some extent, in the dipole segment relaxation region (at temperatures below the glass transition, see Fig.4).[11] The increasing discrepancy between calculation and experiment above the glass transition temperature is not surprising, since we know that in this region the temperature dependence of the relaxation time is no longer a simple exponential but is described by the Williams–Lundell–Fermi equation[30].

By first preparing the electret and then measuring its TSD current (i.e. by carrying out an electret-thermal analysis of the polymer) we obtain not only the characteristics of the electret but also the dielectric relaxation and the molecular mobility characteristics of the polymer. A parallel study of the dielectric relaxation and of the relaxation of

mechanical stresses in the polymer establishes the interrelation between electret and dielectric characteristics and allows the electret-thermal analysis (ETA) thermograms to be interpreted.

Our measurements were carried out with poly(ethylene terephthalate),[31] polycarbonates[32–34], poly(methyl methacrylate) and methacrylate copolymers[35,36] poly(butene terephthalate),[37] poly(vinyl chloride),[38,39] polyamides and poly-imides (see p.193 of Ref.1, and also Refs.40–42), poly(vinyl fluoride) and poly(vinylidene fluoride),[43], polychlorotrifluoroethylene[25], phenol–formaldehyde resins[44], and polyalkane-imide[45].

Like the temperature plots of the dielectric losses, the ETA thermograms include at least two maxima: one in the region of the glass transition temperature, corresponding to dipole segment relaxation, and the other at lower temperatures, corresponding to dipole group relaxation (Fig.4).[32] The TSD current maxima are found at temperatures corresponding to the measurements of dielectric losses at 10^{-3}–10^{-4} Hz frequency. These frequencies are the equivalent frequencies calculated by formula (8). Measurements over a wide range of temperature and frequency (from 10^{6} to 10^{-4} Hz) show that the dielectric constant increment and the shape of the relaxation time distribution function both change with temperature. As the measurement frequency is lowered these relaxation characteristics approach the values given by the ETA. At temperatures above T_g we find a maximum in the TSD current (called the ρ maximum, see above).

In amorphous poly(ethylene terephthalate) (PETP) [31] the ETA thermogram gave one maximum near 60 °C, corresponding to the glass transition in the polymer. An increase in the degree of crystallinity of the sample produces a maximum at 82 °C which characterises the glass transition in the more ordered regions of the amorphous phase (possibly near the boundaries of the crystallites). In oriented crystalline PETP we find only a small maximum near 60 °C, but a large sharp maximum near 82 °C. Thus the relaxation time of the electret hetero-charge τ increases with the crystallinity of the sample, but even in oriented, crystalline PETP τ is small, and the surface charge gradually decays.

Polycarbonate based on *bis*-phenol A is amorphous and has a large residual polarisation[32,46]. The peak temperature on the ETA thermogram for the relaxation of the residual polarisation (α) is quite high (~150 °C), but we also find an additional maximum near 120 °C (α') which results in an immediate decay of charge after polarisation, followed by a long period of charge stability. Crystallisation lowers the secondary maximum α', thus shortening the charge stability time. A small increase in charge stability can be obtained by increasing the molecular weight of the polymer and by stretching the polymer samples to increase their orientation.

Chemical modification of the polymer (by adding triazine groups) increases the stability of the hetero-charges as well as the extent of charging by increasing the polarity of the polymer molccule[34]. The magnitude of the hetero-charge increases with both the polarity and the number of the triazine groups. The addition of norbornane groups[33,34] causes a marked increase in the glass transition temperature of the polycarbonate, thus shortening the stabilisation time of the electrets and offering a useful method of preparing electrets with a large and stable charge[47].

Poly-imides have high glass transition temperatures, and the lifetime of the hetero-charges is large in these materials, but their electrical conductivity (which is electronic) is fairly high at high temperatures[48,49]. Therefore large hetero-charges cannot be obtained in poly-imides. The lifetime of the injected charge is determined by the parameter τ_M, which under ordinary conditions (room temperature and pressure) is only 10^{6}–10^{7} s (which can be contrasted with up to 10^{9} s in polycarbonates.

In polyamides we find[50] that near the glass transition temperature the dielectric constant increment decreases very rapidly with temperature. For this reason the maximum on the ETA thermogram corresponding to randomisation of segment orientations is not usually observed. The strong peak found in the ETA thermogram is due to ionic relaxation of the Maxwell–Wagner type at the interface between the amorphous phase and the crystallites. This maximum appears in the temperature plots of dielectric measurements at frequencies below 1 Hz, and its height increases as the frequency is lowered. On the temperature scale the maximum occurs slightly above the glass transition point (α relaxation temperature). A high degree of crystallinity favours low electrical conductivity, and therefore in some of these materials (for example, polyamide-6,6) the homo-charge is very long-lived[51].

Plasticising treatment of poly(vinyl chloride) lowers the temperature of the TSD current maximum in the region of the glass transition by the same amount as it lowers the glass transition temperature[38]. The addition of plasticisers also lowers the peaks in the region of dipole group losses. A detailed analysis of the results showed that the loss of hetero-charge calculated from the area of the peak in the dipole group loss area is proportional to the increase in the elastic modulus in the temperature range from the maximum of the dipole group loss peak to the maximum of the dipole segment loss peak, i.e. it is proportional to the "deplasticising" effect.

In crystalline polyalkane-imides the dipole segment relaxation maximum decreases because the temperature increment of the dielectric constant falls to such an extent as to be undetectable unless a special technique is used to resolve the TSD current peaks[45]. In this polymer (as in polychlorotrifluoroethylene) a TSD current maximum is found at temperatures above the glass transition: it is associated with the relaxation of dipoles in the crystalline regions (α_c relaxation).

In polychlorotrifluoro-ethylene[25] several maxima are found in the glass transition region. The shape of the ETA thermogram is a function of the technology used in the preparation of the sample, and in particular of the pressure and cooling regime. The position of the maxima in the α_c relaxation region can be used to monitor the changes in polymer structure caused by different preparative regimes. Though PCTFE is a polar polymer, stable electrets (whether hetero-charged or homo-charged) cannot be prepared from it because the glass transition temperature is low and the activation energy of the α_c relaxation is low.

Vulcanised compositions of acrylonitrile and butadiene copolymers contain large (CN) polar groups. The electret hetero-charge resulting from the orientation of these groups is considerable, but the glass transition temperature lies below room temperature and therefore the hetero-charge is stable only at low temperatures. The Maxwell relaxation time is short (though it increases as the concentration of nitrile groups decreases), and therefore the homocharge is also unstable. Evidently, electrets based on vulcanised polar rubbers can be obtained only by carrying out the vulcanisation in an electric field ("chemo-electrets").[52] On the other hand, stable corona electrets can be prepared from vulcanisates of non-polar elastomers (for example, polydimethylsiloxane).[53]

In amorphous polymers such as polycarbonates and polyimides which show a tendency towards structure formation we find (as in PETF) TSD current maxima at temperatures slightly below the glass transition temperature. Experiments

at frequencies between 10^{-1} and 10^{-4} Hz showed that the height of the maximum on the temperature plot (α') increases as the measurement frequency decreases. The height of the maximum increases with heat treatment (annealing), thermal ageing, and exposure to active media[58], which increase the hardness and brittleness of the material and lower its electrical conductivity. In every case the height of the maximum changes in the same sense as the stated parameters. After heat treatment leading to the breakdown of supermolecular formations and to the restoration of the initial properties of the polymer the height of the second maxima (α') of the TSD current also falls.

In partially crystalline polymers (PETF) the α' maximum at ~60 °C decreases as the crystallinity increases. This maximum may be associated with the motion of segments in the disordered regions of the amorphous phase, as opposed to the segments at the boundaries between the amorphous phase and the crystalline regions[31]. The latter have a limited choice of conformations, and their mobility is similarly limited: as a result, the temperature of the TSD current maximum caused by the randomisation of their orientations increases with the crystallinity of the sample.

The height of the maxima at temperatures below 0 °C (dipole group relaxation) is usually less than the value calculated from the increment of the dielectric constant at higher temperatures. This effect is part of the general increase in relaxation rates at higher temperatures.

The temperatures of the TSD current maxima due to dipole relaxation are always consistent with extrapolations of the temperatures of the dielectric loss maxima measured at 10^1 to 10^6 Hz, or with direct measurements at 10^{-3}–10^{-4} Hz frequencies (Fig. 5).

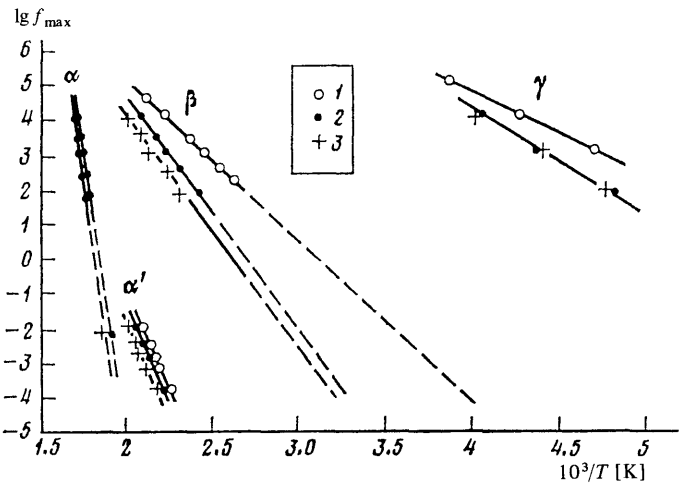


Figure 5. Logarithm of the frequency of the dielectric loss maximum against reciprocal absolute temperature for polyimides (*1* polypyromellitimide, *2* DFO, *3* BZF). The experimental points for $f_{equiv} \approx 10^{-4}$ Hz are obtained from ETA data.

In almost all the ETA thermograms we find, at temperatures higher than the polarisation temperature, a maximum in the TSD current due to the relaxation of bulk charges caused by ionic mobility (the ρ maximum). This maximum is observed, for example, at 120 °C in PETF and at 180 °C in polycarbonate. In some polymers (for example, poly-imides) this maximum is not observed: it is replaced by a monotonic increase in the TSD current due to pyro-electric effects. The height of the ρ maximum depends on the field strength, the polarisation time, and the electrode material.

As formula (14) shows, the measurement of dielectric relaxation by electret-thermal analysis can be used to determine the dielectric loss tangent: in a polymer with $E = 500$ kJ mole^{-1} and $\varepsilon = 3$ (with $E_p = 100$ kV cm^{-1}, $T = 293$ K, $b = 1$ K min^{-1}, and a detector sensitivity of 10^{-14}–10^{-15} A) the result was 10^{-6} (an improvement by two orders of magnitude on the sensitivity of conventional methods of measuring dielectric losses at audio frequencies. Furthermore, the ETA method has an enhanced resolving power due to the lower frequencies at which the measurements are made.

Table 1. Electret and dielectric parameters of a series of polymers.

Polymer	Dielectric measurements				Electret-thermal analysis			Refs.
	T_{max}, °C	Δε	E, kJ mole^{-1}	λ	T_{max}, °C	Δε	W, kJ mole^{-1}	
Dipole segment relaxation								
PC amorph.	175	0.62	586	0.40	147	0.84	197	[11]
PC cryst. (40%)	182	0.28	510	0.26	163	0.44	151	[11]
PETF cryst.	115	0.59	377	0.21	84	0.39	79	[31]
PBTF cryst.	67	1.45	356	0.12	45	1.0	64	[37]
Polysulphone	203	0.59	870	0.35	215	0.55	388	[11]
PI BZF	303	0.63	502	0.47	268	1.78	408	[1, p.193]
Dipole group relaxation								
PC amorph.	−60	0.19	54	0.17	−118	0.17	6 (10)	[11]
PC cryst. (40%)	−65	0.19	54	0.17	−113	0.17	18 (10)	[11]
PBTF cryst.	−56	0.34	67	0.17	−118	0.34	5 (11)	[37]
PETF cryst.	−40	0.5	63	0.20	−110	0.3	8 (13)	[31]
PI BZF	185	0.27	125	0.14	40	0.22	16	[1, p.193]

Notes: T_{max} for the dielectric measurements is the temperature of the ε″ maximum at 1 kHz; the W values shown in brackets were calculated by Eqn. (11), the others by Eqn. (10); PBTF is poly(butene terephthalate), PI is polyimide.

Some results obtained by ETA and by dielectric measurements respectively are compared in Table 1. They relate to a rigid (without air-gap) contact between the electrode and the electret. This type of data can be useful in studies of dipole and molecular mobility in polymers, but under real electret application conditions a gap is almost invariably present (usually, between one charged surface and its counter-electrode). If the TSD currents are measured under these conditions slightly different characteristics are obtained[23]. In particular, the TSD current associated with the ρ maximum often flows in the inverse direction as a result of the decay of the injected charge carriers. In contact-less measurements the quantity determined is often the potential difference V rather than the TSD current. The temperature dependence of V for the electret is an operational characteristic of the electret; the TSD current (measured with an air gap) is proportional to the differential of $V(T)$ with respect to time: $i(T) \propto dV(T)/dt$.[23]

In electrets formed by corona charging or by irradiation with an electron beam (rather than by thermal polarisation) measurements of thermal depolarisation give the parameters

of the traps in which the injected carriers are captured[54,55]. It should be noted, however, that these traps are often emptied by the "unfreezing" of the mobility of the corresponding structure elements, and therefore most of the TSD current peaks occur at the same temperatures as the TSD current peaks of thermo-electrets. Furthermore, the presence of injected charges in the electret gives rise to an electric field in which dipoles can become oriented if the temperature of the sample is raised, and therefore the measured TSD currents are in fact polarisation rather than depolarisation currents. According to formula (4) if $P_0 = 0$ the polarisation in the field of injected charges is proportional to $(\varepsilon_{st} - \varepsilon_\infty)/\varepsilon_{st}$. Experiments of this type on PETP have shown[23] that two maxima appear in the thermogram of corona electrets (the α and the ρ maximum), and that the ratio of their areas is equal to the ratio $\Delta\varepsilon/\varepsilon_{st} = 0.10-0.12$.

Some workers[19,55] do not specially distinguish the current maxima due to polarisation of the electret in the field of the injected charge, and they formally ascribe them to the emission of charge carriers from the traps (which is clearly incorrect). The error of this interpretation was pointed out by McGhie and coworkers[43] (among others) after a detailed study of injection and polarisation currents in poly(vinyl fluoride).

Recent work has shown[24] that the ρ maximum often occurs not at the temperature for which $\tau_M = \tau_{max}$ but at the temperature corresponding to the "unfreezing" of the mobility of the charge carriers at the crystallite boundaries (the α_c relaxation). In polychlorotrifluoro-ethylene, as in poly(vinylidene fluoride), this temperature is ~130 °C. The α_c relaxation is poorly revealed by dielectric measurements at audio frequencies, but it is clearly seen in dynamic mechanical measurements[56]. This was confirmed by our own measurements on poly(ethylene terephthalate), polycarbonate, and poly(vinylidene fluoride).

The dependence of the charges on the field intensity E_p shows a direct proportionality between P and E_p for the α maximum, as expected for dipole polarisation, whereas for the ρ maximum the plot of lg σ_{eff} against $E_p^{1/2}$ is linear, which is typical of injected charge.

We may assume that injected electrons are trapped mainly at the interface between the amorphous and the crystalline phase, where they cause orientation of the surrounding dipoles with a corresponding change in the structure of the polymer. Thus the depth of the trap is determined by the sum of the energies needed to produce the conformational changes in all the surrounding portions of macromolecules resulting from the charge carrier injection. When the electret is heated to the temperature of the α_c relaxation the traps are emptied by the "unfreezing" of the mobility of the charge carriers at the crystallite boundaries.

2. Changes in Polymer Structure Caused by Interaction with an Electric Field

The polarisation of polar polymers causes some changes in the properties and structure of the polymers. Thus, changes in mechanical properties have been reported[57]. The induced elasticity limit $\sigma_{i.e.}$ (fluidity limit) of polycarbonate increases by ~20% in thermo-electrets as compared to the unpolarised polymer. The increase in $\sigma_{i.e.}$ with polarisation time and with field strength, and the decrease in $\sigma_{i.e.}$ during storage, are consistent with the increase or decrease in residual polarisation P_0 (determined by integrating the TSD current). The following relationship is observed:

$$\sigma_{i.e.} = \sigma_0 + CP_0$$

where σ_0 is the induced elasticity limit of the initial polymer, and C is a material constant [$C = 8.82 \times 10^{10}$ N C^{-1} for polycarbonate, $C = 1.09 \times 10^{10}$ N C^{-1} for poly(ethylene terephthalate),[57] and $C = 1.24 \times 10^7$ N C^{-1} for poly(vinyl fluoride)]. The coefficient C has the dimensions of an electrostriction coefficient: it defines the effectiveness of the interaction between the residual polarisation and the mechanical properties of the polymer. The small value of C for poly(vinyl fluoride) reflects the low stability of P_0 at room temperature (at which the measurements of $\sigma_{i.e.}$ were made).

In polycarbonate electrets the velocity of sound is lower and the density is slightly higher than in the initial polymer. These changes can be ascribed to the formation of ordered, denser regions separated by less ordered and less dense regions. Similar changes in structure take place during lengthy heat treatment of the polymers at temperatures close to T_g;[58] these changes are accelerated if the ordering process is assisted by an electric field. The thermophysical properties of the polymer are affected at the same time. A sharp increase in the height of the specific heat maximum (as compared with the unpolarised material) is observed by differential scanning calorimetry on the thermograms of electrets near T_g. For example, in poly(vinyl chloride) the enthalpy ΔH increases 1.5-fold. This thermal effect is due to the breakdown of the residual polarisation[50].

Table 2. Piezo-electric properties of polymer electrets.

Polymer	T_p, °C	E_p, kV cm^{-1}	t_p, h	d_{31}, pC N^{-1}	d_{33}, pC N^{-1}	τ*, days	Refs.
PC amorph.	145	300	2	0.10	0.10	254	[10, 67]
PC cryst. (40%)	145	200	3	0.11	0.10	10^3	[10]
PA-11	—	—	—	0.5	—	10^3	[67]
PA-12	160	60	2	0.11	0.2	2	[10]
PA-6,6	160	60	2	0.11	0.3	—	
PVC	80	250	2	1.7	1.7	$1.1 \cdot 10^5$	[10, 62]
PAN	115	200	2	0.62	4.1	640	[62]
PETF amorph.	100	100	2	1.5	—	0,06	[10]
PETF cryst.	120	200	3	0.01	—	—	[10]
PVF	83	220	2	2.2	4.0	500	[76]
PVDF α form	90	100	2	0.66	2.7	10^3	[76]
PVDF β form (60% cryst.)	80	600—1000	0.5	15—25	6.3—20	10^5	[76]
PVDF with additions of LTZ** (21 vol%)	120	120	0.5	4.2	—	—	[83]
Poly-3,3(dichloro-methyloxycyclo-butane)***	120	250	1	30	—	—	[66]

*Relaxation time of the piezo-modulus d.
**Lead titanate zirconate.
***Pentaplast, or Pentone.

Mechanical deformation of polar polymers produces mechano-electrets[1,59-63] in which the size of the charge increases with the degree of deformation. Mechano-electrets have well developed piezo-electric properties[62], stronger than those of thermo-electrets made from the same polymers[63]. The orientation of the macromolecules during deformation induces a preferred orientation of the dipoles (with their polar groups normal to the deformation plane). The increases in the induced elasticity limit and in the mechanical strength of the polymer samples resulting from polarisation[57] are the inverse effects of the formation of mechano-electrets.

In crystalline polymers [poly(vinylidene fluoride), polyamide-11] changes in structure of the crystallites can be produced by a polarising field. In poly(vinylidene fluoride) the crystalline α form is converted into the β form[64] by the rotation of the dipoles (CF_2 groups) round the axis of the macromolecule chain. A theoretical analysis[65] has shown that this rearrangement is assisted by the simultaneous rotation of all the CF_2 groups in the chain, which gives the lowest total free energy. The dependence of the polarisation P on the field strength E_p for a slowly changing field (10^{-1}–10^{-4} Hz) has a typical relaxation form with a hysteresis loop (as in ferroelectric materials). Similar electret properties have been reported for poly-3,3-*bis*-chloromethyloxyethane (Pentaplast),[66] polyamide-11,[67] and the copolymers of vinylidene fluoride and trifluoro-ethylene[68,69].

Unfortunately, studies of hysteresis phenomena have not been made on other polymers. In view of the relaxation form of the molecular mobility we may assume that ferroelectric phenomena are present to a greater or lesser extent in all polar polymers.

Changes in structure of polyacrylonitrile after polarisation have been studied by i.r. spectroscopy and X-ray structural analysis[61]. This work has revealed ordering effects in the segments and an increase in the density of ordered regions. Similar effects were observed when the sample was annealed without an electric field, but in a lesser degree. The authors point out[61] the similarity between the changes in structure of polyacrylonitrile and those of polycarbonate[57].

IV. PIEZO- AND PYRO-ELECTRIC PROPERTIES OF ELECTRETS

1. Piezo-electricity in Polymer Electrets

The piezo-effect in electrets[70–81] is due to the change in the surface charge density caused by deformation of the polymer[70]:

$$d_{33} = \frac{dP}{dF} - 2\eta \frac{\sigma_{eff}}{E_{el}} \qquad (15)$$

where F is the load, η is Poisson's ratio, E_{el} is the elastic modulus, and d_{33} is the piezo-modulus of the planar polymer electret under compression (the polarisation axis is assumed to coincide with the deformation axis "3").

Experiments on ceramic electrets have shown that the second term of Eqn.(15) is too small to account for the observed piezo-effect. However, in polymer electrets the elastic modulus is small, and in rubber "chemo-electrets" the piezo-effect is fully accounted for by the second component[52,71].

Later work with a large number of polymers (see p.145 of Ref.1) showed that the piezo-effect tends to increase with the polarity of the polymer, whereas its stability increases with the rigidity of the macromolecular chain. A theoretical analysis[10] demonstrated that if the dielectric constant is unaffected by the deformation (i.e. if the electrostriction coefficient is small) the piezo-modulus under expansion d_{31} reflects exclusively the changes in geometric shape of the sample, and is given by

$$d_{31} = -(1-\eta) P_0/E_{el}$$

whereas under compression

$$d_{33} = -2\eta P_0/E_{el} . \qquad (16)$$

These relationships are useful for predicting the practical value of electret devices based on the piezo-electric properties of polymers. Knowing E_{el} and the P_0 value given by integration of the TSD current or calculated by formula (7) we can find the piezo-modulus. Calculated and experimental values of the piezo-modulus d_{31} are compared in Table 2.

Broadhurst and Davies[72] allowed for the Onsager internal field. Assuming that the formation of residual polarisation orients the dipoles along the field at an average angle θ to the direction of the polarising field, they obtained the expression for P_0

$$P_0 = (\varepsilon_\infty + 2) N\mu_0 \langle \cos\theta \rangle / 3 \qquad (17)$$

which gave the formula for $d = dP_0/dF$

$$d = -P_0 \frac{\varepsilon_\infty}{3} \alpha \qquad (18)$$

where α is the volume compressibility. Since under compression $\alpha = (1/V)(dV/dE) = 2\eta/E_{el}$, and since $\varepsilon_\infty \cong 3$ for poly(vinyl chloride), for which formula (18) has been shown to be valid[73], we arrive at an expression identical to Eqn.(16).[10]

Eqns.(16) and (17) are convenient for electrets with a residual polarisation consisting of oriented and "frozen" dipoles. It is found experimentally[74] that non-polar polymers with an injected homo-charge σ_p also show a piezo-effect, especially under flexural deformation, though the piezo-modulus is small.

In poly(vinylidene fluoride) the piezo-effect is so large as to require special discussion. Poly(vinylidene fluoride) (PVDF) is a polar polymer characterised [like poly(vinyl fluoride)] by a low glass transition temperature (below room temperature). Therefore under normal conditions the polymer in the amorphous phase is in a highly elastic state, and thermo-electrets made from this material are unstable. Injected charge carriers (homo-charges) are captured in traps at the boundary between the amorphous and the crystalline phase, from which they can be freed only by the "unfreezing" of the mobility of the macromolecules on the crystallite surfaces (α_c relaxation). This effect is confirmed by dynamic mechanical measurements[24], and is analogous to the corresponding process in polytetrafluoro-ethylene (a typical electret material).

We can assume that charge carriers trapped near the surface can survive for a long time ($\geq 10^{10}$ s), and generate a strong internal field in which the dipoles are oriented[10]. The application of a mechanical load to a dielectric with oriented dipoles produces a piezo-effect whose magnitude depends on the injected charge σ_p (measured by integrating the TSD current in the region of the α_c relaxation), on the depth of injection l, on the sample thickness L, and on the polarisability (defined as $\Delta\varepsilon = \varepsilon_{st} - \varepsilon_\infty$). The piezo-modulus under expansion is

$$d_{31} = \frac{(1-\eta)}{E_{el}} \frac{\Delta\varepsilon(\alpha)}{\varepsilon_{st}} \sigma_p \frac{l}{L+l} .$$

Inserting $l = 1$ μm with $L = 20$ μm and $\varepsilon_{st} = n_\lambda^2 + \Delta\varepsilon(\alpha) = 2.2 + 6.2 = 8.4$ for a non-oriented film of PVDF in its less polar, crystalline σ form, with $\sigma_p = 0.057$ C m^{-2} and $E_{el} = 1.1 \times 10^9$ Pa, we obtain $d_{31} = 1$ pC N^{-1}. After orientation the parameter $\Delta\varepsilon(\alpha)$ increases to 8–11, and σ_p increases to 1.48 C m^{-2} for polarising fields up to 450 kV cm^{-1}. In this case d_{31} increases to 22–30 pC N^{-1}, which corresponds to the highest experimentally observed values of d_{31}.

This theoretical model by allowing for the role of injected charges brings all the polymer electrets into a coherent group. It can be used to calculate the change in structure of PVDF in an electric field in terms of changes in ε only. Similar views have been expressed by other workers[67,76,77].

However, wide acceptance has been gained by the view[78–80] that the piezo-effect in PVDF and in the copolymers of vinylidene fluoride is due mainly to spontaneous polarisation

in the crystallites of the β form, which is formed from the crystalline α form by the orienting effect of stretching the sample or under the influence of very strong electric fields ($\sim 10^8$ V m^{-1}).

Other workers[74,81] have allowed for the crystallites of the polar, spontaneously polarised β form dispersed in the amorphous matrix as well as for the change in dielectric constant produced by the deformation. This approach gave the following expression for the piezo-modulus d in PVDF:

$$d = \frac{P_0}{E_{el}}\left[\frac{\varepsilon_{cr}}{2\varepsilon+\varepsilon_{cr}}\left(\frac{\varkappa}{\varepsilon}-\frac{\varkappa_{cr}}{\varepsilon_{cr}}h\right)+2\eta\right]+v\left(\frac{3\varepsilon}{2\varepsilon+\varepsilon_{cr}}\right)h \qquad (19)$$

where the subscript "cr" refers to the polymer in the crystalline form, v is the volume fraction of the crystalline phase, $h = 5E_{el}/[3E_{el} + 2E_{el}(cr)]$, and $\varkappa$ is the electro-striction coefficient, equal to $E(\partial\varepsilon/\partial F)$. The calculation shows that the component d [due to the change in shape of the sample and related to the Poisson ratio by Eqn.(19)] accounts for ~78% of the piezo-effect[81]. However, the parameter P_0 is identified[81] with the spontaneous polarisation of the electret in the crystalline β form rather than with the polarisation in the field of the injected charge.

Thus the piezo-effect in polymer electrets may be due to the change in surface density of the homo-charge caused by deformation ($d\sigma_p/dF$), the change in density of the residual polarisation P_0 (dP_0/dF), or the "true" piezo-effect in the spontaneously polarised particles (in PVDF these particles consist of polarised crystallites of the β phase).

These spontaneously polarised particles need not even (in general) be particles of the polymer: they could be introduced as a powdered inorganic ferro-electric. In this case the piezo-electric properties of the resulting composite materials can be extremely high. By combining a suitable content of ferro-electric powder with a polymer having adequate polarity and intrinsic piezo-electric properties materials with very favourable characteristics have been obtained[82-85]. The production of polymeric or composite piezo-elements is incomparably simpler than the preparation of ceramic devices, and the piezo-sensitivity per stage of the former ($g_{33} = d_{33}/.\varepsilon\varepsilon_0$) is 10–100 times greater than in the ceramic ferro-electric devices because of the lower ε values in polymers.

2. Pyro-electricity in Polymer Electrets

Pyro-electricity appears as a result of changes in polarisation P or in the density of injected charges produced by changes in temperature.

The pyro-coefficient p, which characterises the change in charge density of the dielectric produced by a change in temperature of one degree, is directly proportional to P_0 and to the volume thermal expansion coefficient α:[73]

$$p = -\frac{\varepsilon_\infty}{3}\alpha P_0 .$$

The pyro-effect associated with σ_p is usually small. In the case of polymers containing a ferro-electric component [poly(vinylidene fluoride)] the pyro-effect is described by a formula derived from a mixture of a ferro-electric and a non-polar substance[81]:

$$p = P_0\left[\frac{\varepsilon_{cr}}{2\varepsilon+\varepsilon_{cr}}\left(\frac{\lambda}{\varepsilon}-\frac{\lambda_{cr}}{\varepsilon_{cr}}\right)-\beta\right]+v\left(\frac{3\varepsilon}{2\varepsilon+\varepsilon_{cr}}\right)P \qquad (20)$$

where $\lambda = \partial\varepsilon/\partial T$ is the temperature coefficient of the dielectric constant, and β is the linear thermal expansion coefficient. It was found experimentally that the component of p due to the volume change [and associated with the coefficient β in Eqn.(20)] makes a 50% contribution to the pyro-effect in PVDF.

Composite materials based on polymers with added ferro-electrics offer large values of the pyro-coefficient p. Some recent results are summarised in Table 3.

V. APPLICATIONS OF POLYMER ELECTRETS

Electrets can find applications: 1) as dielectrics, with an added external electric field, 2) as dielectrics, with an internal polarisation, 3) as piezo-electric materials, and 4) as pyro-electric materials.

Table 3. Pyro-electric properties of polymer electrets.

Polymer	E_p, kV cm^{-1}	T_p, °C	$10^5 p$, C m^{-2}K^{-1}	Refs.
PVC	320	90	0.11	[73]
PAN	215	109	0.054	[73]
PAN	—	—	3.9	[96]
PVDF, not oriented, α-form	300	100	2.4	[76]
PVDF, uniaxially oriented, β-form	2200	20	2—20	[76]
PVDF, biaxially oriented, β-form	2200	20	2,7—8.0	[76]

As dielectrics (with an external electric field) electrets are widely used in filters, for controlling electron beams (and in particular for focussing electron beams), and in electro-mechanical transducers (microphones, pick-ups, etc.). The most widely used of these devices is the electret condenser microphone, currently manufactured on a scale of millions per annum. The use of electrets has greatly simplified microphone design, allowing a reduction in size to ~5 mm coupled with improved properties (for example, the linearity region of industrially produced electret microphones extends from 50 to 16000 Hz).[2,86-88] Special electret microphones for studying ultrasound and infrasound have also been described[89]. Electret fibre filters[90], developed outside the Soviet Union under the name "filtret",[91] are now widely used: they are cheap, much more efficient than previous fibre filters, and they offer excellent protection against airborne industrial or radioactive dust.

The incidence of thrombosis has been reduced by using artificial blood vessels and artificial heart components with electret properties[92].

In their second function electrets can be used as a very special type of electric cell. A temperature rise (for example, in a fire alarm device) may give a TSD current sufficient to activate a radio transmitter (see p. 204 of Ref.1).

As piezo-electric materials[93] polymer electrets have been used in stereo headphones, acoustic pick-ups[94], and igniters, and also in fans. Over 40 different applications of piezo-electric poly(vinylidene fluoride) polymer film have already been patented[76]. Applications in hydro-acoustics, in switching systems for fibre optics, in the generation of focussed ultrasonic signals, and in the prevention of fouling of ships' hulls by marine plants and molluscs[95] are especially interesting.

Likely future pyro-electric applications of polymer electrets (for example, based on acrylonitrile) include the direct conversion of solar into electrical energy[96], night viewing with infrared radiation [poly(vinylidene fluoride)], and various forms of pyro-electric detector and other devices[76,93].

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In conclusion we note that the prospects of more widespread applications of polymer electrets are good. New uses are being discovered every year, in very different branches of technology. We should also stress that only a small number of polymer electret materials has been exploited in practice so far. For the production of external electric fields the following materials have been used most widely: polytetrafluoro-ethylene, the tetrafluoro-ethylene–hexafluoropropene copolymer, polycarbonate, and poly(methyl methacrylate), whereas polypropene, poly(chlorotrifluoroethylene), and poly(methyl siloxane) are beginning to find practical applications. Materials used in practical piezoelectric devices include poly(vinylidene fluoride), poly(vinyl chloride), and composite polymer materials containing a ferro-electric ceramic filler (lead titanate zirconate).

We can expect practical applications of polymer electrets in pyro-electric devices, and the development of an increasingly wide range of polymers for use in electric field generators and in piezo-electric devices (polyamides, polysulphones, and vinylidene fluoride copolymers[97]). Further developments in the modification of the physico-mechanical properties of polymers by the application of electric or magnetic fields can also be expected.

The study of the influence of an external electric field on the structure of polymer electrets is still in its initial stages[98,99].

REFERENCES

1. G.A.Lushcheikin, "Polimernye Elektrety" (Polymer Electrets), Izd.Khimiya, Moscow, 1976.
2. A.N.Gubkin, "Elektrety" (Electrets), Izd.Nauka, Moscow, 1978.
3. M.M.Perlman (Editor), "Electrets", Electrochemical Society, Princeton, 1973.
4. A.N.Gubkin and V.A.Ogloblin, Symposium "Elektretnyi Effekt i Dielektricheskaya Relaksatsiya" (The Electret Effect and Dielectric Relaxation), Izd.MIEM, Moscow, 1979, p.150.
5. J.Mrazek, Acta Technica CSAV, 1972, **4**, 402.
6. M.Latour, J.Appl.Phys., 1975, **46**, 42.
7. V.K.Shatalov and G.A.Lushcheikin, "Materialy Pyatogo Vsesoyuznogo Simpoziuma po Mekhanokhimii i Mekhanoemissi Tverdykh Tel" (Proceedings of the Fifth All-Union Symposium on the Mechano-chemistry and Mechano-emission of Solids), Vol.1, Izd.Akad. Nauk EstSSR, Tallin, 1977, p.139.
8. J.Asano and T.Suzuki, J.Appl.Phys., 1978, **44**, 1378.
9. V.K.Shatalov and G.A.Lushcheikin, "Materialy Vsesoyuznoi Konferentsii Fizika Dielektrikov i Perspektivy Ee Razvitiya" (Proceedings of the All-Union Conference on the Physics of Dielectrics and Its Likely Future Developments), Vol.2, Izd.LPI, Leningrad, 1973, p.156.
10. G.A.Lushcheikin and Kh.D.Dzhumanbaev, Plast. Massy, 1977(10), 7.
11. G.A.Lushcheikin, Plast.Massy, 1979(2), 31.
12. W.Reddish, Symposium "Transitions and Relaxation Processes in Polymers" (Translated into Russian), Izd.Mir, Moscow, 1968, p.138.
13. B.I.Sazhin (Editor), "Elektricheskie Svoistva Polimerov" (Electrical Properties of Polymers), Izd. Khimiya, Leningrad, 1977.
14. V.P.Shuvaev, B.I.Sazhin, and V.S.Skurikhina, Vysokomol.Soed., 1975, **17A**, 1058.
15. D.M.Taylor and T.J.Lewis, J.Phys.D: Appl.Phys., 1971, **4**, 1346.
16. E.B.Fainshtein, G.A.Lushcheikin, and L.A.Igonin, Vysokomol.Soed., 1974, **16A**, 1677.
17. T.Fabish, J.Appl.Phys., 1980, **51**, 1247.
18. M.I.Kornfel'd, Fiz.Tverdogo Tela, 1975, **17**, 1696.
19. G.M.Sessler and J.E.West, J.Appl.Phys., 1972, **43**, 922.
20. M.E.Borisova, S.N.Koikov, V.A.Paribok, and V.A.Fomin, Vysokomol.Soed., 1975, **17B**, 488.
21. V.P.Sichkar', S.E.Vaisberg, and V.A.Karpov, Vysokomol.Soed., 1971, **13B**, 679.
22. B.A.Cresswell, B.I.Gribbon, M.A.Kabayama, and M.M.Perlman, Telesis, 1971, **2**(1), 21.
23. G.A.Lushcheikin and A.G.Dzhabarov, "Doklady Sed'mogo Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel" (Proceedings of the Seventh All-Union Symposium on the Mechano-emission and Mechano-chemistry of Solids), Vol.1, Izd.Ukituvich, Tashkent, 1981, p.31.
24. G.A.Lushcheikin and A.G.Dzhabarov, "Tezisy Dokladov Vos'mogo Vsesoyuznogo Simpoziuma po Mekhanoemissii i Mekhanokhimii Tverdykh Tel" (Abstracts of Papers Presented to the Eighth All-Union Symposium on the Mechano-emission and Mechano-chemistry of Solids), Izd.Akad.Nauk EstSSR, Tallin, 1981, p.44.
25. K.S.Firsova, G.A.Lushcheikin, A.Ya.Malkin, L.I.Voiteshonok, A.P.Kiselev, V.I.Serenkov, L.A.Zezina, and L.A.Igonin, Vysokomol.Soed., 1978, **20A**, 2730.
26. J.H.Calderwood, J.Phys.D: Appl.Phys., 1978, **11**, 781.
27. Yu.A.Gorokhovatskii, "Osnovy Termodepolyarizatsionnogo Analiza" (Fundamentals of Thermal Depolarisation Analysis), Izd.Nauka, Moscow, 1981.
28. V.N.Vertoprakhov and E.G.Sal'man, "Termostimulirovannye Toki v Neorganicheskikh Veshchestvakh" (Thermally Stimulated Currents in Inorganic Substances), Izd.Nauka, Novosibirsk, 1979.
29. J.Turnhout, Topics Appl.Phys.(Electrets), 1980, **33**, 114.
30. I.I.Perepechko, "Akusticheskie Metody Issledovaniya Polimerov" (Acoustic Methods in Studying Polymers), Izd.Khimiya, Moscow, 1973.
31. G.A.Lushcheikin and L.I.Voiteshonok, Vysokomol. Soed., 1975, **17A**, 429.
32. G.A.Lushcheikin and L.I.Voiteshonok, Vysokomol. Soed., 1974, **16A**, 1364.
33. G.A.Lushcheikin, O.V.Smirnova, M.K.Polevaya, V.M.Gladyshev, and G.I.Sidorova, Vysokomol.Soed., 1976, **18B**, 174.
34. G.A.Lushcheikin, L.I.Voiteshonok, O.V.Smirnova, V.N.Bolmosova, L.L.Vladimirova, and M.K.Polevaya, Plast.Massy, 1977(10), 9.
35. G.A.Lushcheikin and V.K.Shatalov, Plast.Massy, 1973(2), 45.
36. J.Turnhout, "Thermally Stimulated Discharge of Polymer Electrets", Elsevier, Amsterdam, 1975.
37. G.A.Lushcheikin, V.S.Kolerov, and M.K.Polevaya, Plast.Massy, 1976(10), 65.
38. G.A.Lushcheikin, Kh.D.Dzhumanbaev, and R.S.Barshtein, Vysokomol.Soed., 1980, **22B**, 751.
39. P.Hedvig, "Dielectric Spectroscopy of Polymers", Halsted Press, New York, 1977.
40. G.A.Lushcheikin and B.A.Gringut, Vysokomol.Soed., 1972, **14B**, 53.
41. G.A.Lushcheikin, V.V.Surova, V.D.Vorob'ev, M.L.Dobrokhotova, and L.N.Emel'yanova, Vysokomol. Soed., 1975, **17B**, 159.

42. G.A.Lushcheikin, V.V.Surova, B.A.Gringut, L.V.Emel'yanova, M.L.Dobrokhotova, and V.D.Vorob'ev, Plast.Massy, 1972(8), 28.
43. A.R.McGhie, G.McGibbon, A.Shurplis, and E.J.Stanley, Polymer, 1972, **13**, 371.
44. E.E.Alekseev, G.A.Lushcheikin, L.V.Makarova, L.I.Voiteshonok, and L.A.Igonin, Dep.VINITI No.21-36/78.
45. G.A.Lushcheikin, G.A.Chernova, Kh.D.Dzhumanbaev, V.V.Shmel'kova, N.K.Pinaeva, and V.D.Vorob'ev, Vysokomol.Soed., 1980, **22B**, 153.
46. G.A.Lushcheikin and M.K.Polevaya-Mansfel'd, Plast. Massy, 1971(2), 34.
47. G.M.Sessler, Topics Appl.Phys.(Electrets), 1980, **33**, 4.
48. E.B.Fainshtein, G.A.Lushcheikin, and L.A.Igonin, Vysokomol.Soed., 1974, **18A**, 1677.
49. E.B.Fainshtein, L.A.Igonin, and G.A.Lushcheikin, Vysokomol.Soed., 1976, **18A**, 580.
50. G.A.Lushcheikin and Kh.D.Dzhumanbaev, Dep.TsNII "Elektronika", No.4431/76.
51. J.Vanderschueren, M.Ladang, and J.M.Heuschen, Macromolecules, 1980, **13**, 973.
52. V.E.Gul', G.A.Lushcheikin, and V.M.Fridkin, Kristallografiya, 1962, **7**, 797.
53. K.J.Kao, T.J.Lewis, and M.M.Perlman, J.Appl. Phys., 1979, **50**, 8181.
54. M.M.Perlman, K.J.Kao, and S.S.Bamji, J.Appl. Phys., 1979, **50**, 3622.
55. M.M.Perlman, J.Electrochem.Soc., 1972, **119**, 892.
56. J.D.Hoffman, G.Williams, and E.Passaglia, in "Transitions and Relaxations in Polymers" (Edited by R.F.Boyer), Interscience, New York, 1966 (Translated into Russian), Izd.Mir, Moscow, 1968, p.193.
57. G.A.Lushcheikin, V.E.Gul', V.K.Shatalov, G.A.Tsoi, and I.G.Kuznetsova, Dokl.Akad.Nauk SSSR, 1975, **225**, 801.
58. Cotis A.Conde and T.A.Menson, Amer.Chem.Soc., Polymer Prepr., 1974, **15**, 465.
59. M.Latour, J.Electrostatics, 1976, **2**, 41.
60. S.I.Stupp and S.H.Carr, J.Appl.Phys., 1975, **46**, 4120.
61. S.I.Stupp and S.H.Carr, Colloid and Polymer Sci., 1979, **257**, 913.
62. J.Cohen and S.Edelman, J.Appl.Phys., 1971, **42**, 3072.
63. J.Cohen and S.Edelman, J.Appl.Phys., 1971, **42**, 893.
64. G.T.Davies, J.E.McKinney, M.G.Broadhurst, and S.C.Roth, J.Appl.Phys., 1978, **49**, 4998.
65. M.G.Broadhurst, G.T.Davies, J.E.McKinney, and R.E.Collins, J.Appl.Phys., 1978, **49**, 4992.
66. J.Fujimori and H.Izumi, Jap.P.79-120900(1979); Chem.Abs., 1979, **92**, 53005.
67. E.Fukada, Progr.Polymer Sci.(Japan), 1971, **2**, 329.
68. N.Murayama, Polymer Sci., Polymer Phys.Ed., 1976, **13**, 929.
69. N.Koizumi, Reports Progr.Polymer Phys.Japan, 1981, **24**, 403.
70. A.N.Gubkin and V.S.Sorokin, Izv.Akad.Nauk SSSR, Ser.Fiz., 1960, **24**, 246.
71. P.T.A.Klaase and J.Turnhout, "Proceedings of the Third International Conference on Dielectric Materials Measurements and Applications" (Birmingham, 1979), IEE Conference Publications, London, 1979, p.411.
72. M.G.Broadhurst and G.T.Davies, Topics Appl. Phys.(Electrets), 1980, **33**, 289.
73. F.I.Mopsik and M.G.Broadhurst, J.Appl.Phys., 1975, **46**, 4204.
74. R.Haykawa and J.Wada, Adv.Polymer Sci., 1973, 1.
75. G.A.Lushcheikin, Symposium "Ul'trazvuk" (Ultrasound), Izd.Sovetskaya Entsiklopediya, 1979, p.377.
76. G.M.Sessler, J.Acoust.Soc.Amer., 1981, **70**, 1569.
77. P.E.Bloomfield, R.A.Ferren, P.F.Radice, H.Stefanou, and O.S.Sprout, Naval Res.Rev., 1978, **31**, 1.
78. R.G.Kepler and R.A.Anderson, J.Appl.Phys., 1978, **49**, 4918.
79. N.Takahushi and A.Odajama, Ferroelectrics, 1981, **32**, 49.
80. M.G.Broadhurst and G.T.Davies, Ferroelectrics, 1981, **32**, 177.
81. J.Wada and R.Haykawa, Ferroelectrics, 1981, **32**, 115.
82. R.Z.Kleine and E.Zh.Freidenfel'd, Symposium "Segneto- i P'ezomaterialy i Ikh Primenenie" (Ferroelectric and Piezoelectric Materials and Their Applications), Izd.MDNTP, Moscow, 1978, p.131.
83. T.Furukawa, K.Ishida, and E.Fukada, J.Appl.Phys., 1979, **50**, 4904.
84. G.A.Lushcheikin and V.M.Petrov, Symposium, "Poluchenie i Primenenie Segneto- i P'ezomaterialov v Narodnom Khozyaistve" (Production and Uses of Ferroelectric and Piezoelectric Materials in the National Economy), Izd.MDNTP, Moscow, 1981, p.8.
85. R.E.Newham, D.P.Shinner, K.A.Klicker, A.S.Bhalla, B.Hadiman, and T.R.Guiraja, Ferroelectrics, 1980, **27**, 49.
86. P.V.Murphy and F.W.Fraim, in "Electrets" (Edited by M.M.Perlman), Electrochemical Society, Princeton, 1973, p.603.
87. E.K.Gorbunova, A.I.Kozlova, E.L.Seisyan, and V.N.Tairov, Akust.Zhur., 1975, **20**, 377.
88. G.M.Sessler and J.E.West, "Proceedings of the Seventeenth International Congress on Acoustics", Budapest, 1971, p.413.
89. A.R.Watson, J.Eng.Soc., 1973, **21**, 719.
90. Y.Wada, M.M.Perlman, and H.Kokado, "Charge Storage, Charge Transport and Electrostatics with their Applications", Elsevier, Amsterdam, 1979.
91. J.Turnhout, J.H.M.Albers, W.J.Hoeneveld, J.W.C.Adamse, and L.M.Rossen, "Papers Presented to the Fifth Conference on Electrostatic Phenomena, Oxford, 1979", Institute of Physics, Bristol–London, 1979.
92. G.V.Efashkin and A.K.Chepurov, Symposium, "Elektretnyi Effekt i Elektricheskaya Relaksatsiya" (The Electret Effect and Electrical Relaxation), No.1, Izd.MIEM, Moscow, 1979, p.226.
93. M.A.Marcus, Ferroelectrics, 1982, **70**, 1569.
94. M.Tamura, J.Audio Eng.Soc., 1975, **23**, 21.
95. M.Latour and P.Murphy, Ferroelectrics, 1981, **32**, 33.
96. V.S.Likhovidov, V.V.Golovanov, and A.V.Vannikov, Vysokomol.Soed., 1978, **20A**, 71.
97. T.Furukawa, G.E.Johnson, H.E.Bair, Y.Tajitsu, A.Chiba, and E.Fukada, Ferroelectrics, 1981, **32**, 61.
98. A.D.Stadnik and F.D.Miroshnichenko, in "Sbornik Trudov Kievskogo Gosudarstvennogo Pedagogicheskogo Instituta Imeni M.Gor'kogo" (Collected Papers from the Gor'kii Kiev State Educational Institute), 1976, p.141.
99. A.D.Stadnik and F.D.Miroshnichenko, Dep.VINITI, No.3655/76.

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