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PYROELECTRICITY AND CHARGE TRANSPORT IN A COPOLYMER OF VINYLIDE--ETC(U)
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Pyroelectricity and Charge Transport in a Copolymer of
Vinylidene Fluoride and Tetrafluoroethylene

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ABSTRACT

A copolymer of vinylidene fluoride and tetrafluoroethylene shows pyroelectric and piezoelectric effects after poling. Thermal pulsing measurements indicate that the polarization in this material is highly non-uniform. The piezo/pyroelectric response of this non-uniformly poled copolymer consists of two parts--a rapid response that is the result of changes in internal polarization, and a delayed response due to reversible motion of real charge through the bulk of the material. This model explains previously reported observations of the independence of pyroelectric response over a wide range of poling conditions.

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I. INTRODUCTION

Several mechanisms have been suggested to explain the origin of piezoelectricity and pyroelectricity in polymer films [1]. One model, in particular, accounts for the experimentally observed results from polyvinylidene fluoride (PVDF) in terms of aligned molecular dipoles within crystalline lamellae subjected to dimensional change, dipole orientation fluctuations and electrostriction [1]. More recently, a co-operative ferroelectric model has been developed to explain the polarization process and the broad features of polarization switching under high electric fields [2].

The alignment of dipoles through reorientation within crystalline regions under an applied field finds experimental support from infrared and x-ray data on β -phase PVDF [3,4] as well as from field-induced crystal phase changes in initially α -phase crystals [5-10].

Closely related to questions on the origin of the electrical response are those pertaining to the uniformity of polarization through the thickness of the material. Some authors [11,12] have postulated that interfacial effects are very important in understanding certain properties of ferroelectric materials. Others have shown experimentally that more uniform polarization in PVDF occurs at high electric fields, high temperatures and long poling times [13]. In general, our results confirm an essentially uniform polarization in "well poled" PVDF films. A particular type of vinylidene fluoride--tetrafluorethylene copolymer, however, exhibits non-uniform polarization over the range of poling conditions that the material can tolerate without electrical breakdown.

This paper presents evidence for non-uniform polarization in this material, and discusses certain effects in the piezoelectric and pyroelectric response that result from it. The existence of non-uniform polarization implies that significant space charge is present in the polymer during poling, resulting in a substantial departure from uniform electric field conditions.

II. EXPERIMENTAL

A. Sample Preparation

The copolymer studied in this work was 73 weight percent vinylidene fluoride and 27 weight percent tetrafluoroethylene supplied as a powder by the Pennwalt Corporation [14]. The powder was evacuated, compressed, and melted in a pellet-making mold commonly used for infrared sample preparation. Portions of the pellet were subsequently melted and pressed between sheets of polyimide to prepare films typically 30 to 50 μm thick and 3 cm in diameter. Depending on the rate of cooling from the melt, the degree of crystallinity could be varied from 35 percent (when quenching in ice water) to 50 percent (when crystallized isothermally for 48 hours at 118 $^{\circ}\text{C}$).

Films to be poled were provided with metal electrodes (gold or aluminum) on both sides by vacuum evaporation. Samples were poled at constant temperature and with a fixed applied voltage. For samples poled above room temperature the sample was quenched in ice water after the desired poling time, and the electric field was removed within one minute after quenching.

B. Measurements

Three kinds of measurements were performed: (1) The short circuit current was measured while the sample temperature changed slowly, (2) the charge was measured as a function of time following a rapid (seconds) step in bath temperature, and (3) the transient was measured during temperature equilibration of the sample following a heat pulse of a few μs duration applied to the sample surface. Pyroelectric response from a sample of slowly changing temperature was measured as previously described [15]. Briefly, the sample was placed in a copper cell in intimate contact with its bottom and the temperature was changed at a nearly constant rate of 0.4 K/min for about 3 minutes. The current flowing in the external circuit between the electrodes on the surfaces of the film was amplified and recorded as a function of time. The temperature was simultaneously recorded.

The pyroelectric coefficient was obtained from the expression

$$p_y = i/[A(dT/dt)] \quad (1)$$

where p_y is the pyroelectric coefficient (C/cm²K),

i is the current (A),

dT/dt is the rate of temperature change (K/s)

and A is the electrode area (cm²).

Equation (1) is valid only if the temperature dependent background current generated by the sample is negligible. If this condition is satisfied, the measured current should become zero when dT/dt is zero. When a background current is present, the sample current continues to change as the temperature changes, asymptotically approaching the background current at long times. Background currents were only a few percent of the pyroelectric currents in the results discussed here and, when present, were removed from the data before applying equation (1).

The pyroelectric response of typical co-polymer samples was observed to lag behind changes in temperature. For example, some time elapsed after the rate of temperature change, dT/dt , became constant before the current reached a

constant value. This is contrary to what is expected from equation (1) and contrary to what is observed for polyvinylidene fluoride homopolymer samples. The pyroelectric response was therefore measured in another way--by subjecting the polymer to a step-like temperature change.

In this second set of measurements, the sample is totally immersed in a continuously stirred beaker of n-hexane. A temperature change, ΔT , of about 1K is produced by adding a small amount of chilled or heated liquid. This change takes place in about one second. The pyroelectric response is measured under approximately short-circuited conditions with a charge amplifier.

The time scale of this temperature change is such that the temperature in the polymer at any instant of time is essentially spatially uniform. The charge response, $Q_{s.c.}$, of the polymer is obtained from equation (1) by integration:

$$Q_{s.c.} = A p_y \Delta T \quad (2)$$

It should be noted that the measurements described so far in this section are designed to minimize temperature gradients in the sample. The quantity, p_y , in eq's. (1) and (2) is therefore an average value of a quantity which may vary across the thickness in the absence of charge motion within the polymer. In the context of a model of aligned electrostatic dipoles within the polymer [1], p_y is a measure of the mean value P_m of polarization $P(x)$ in the sample, where x is a position co-ordinate representing distance from one surface of the sample, $P_m = (\int_0^d P(x)dx)/d$, and d is the sample thickness.

More information about the spatial distribution of polarization through the sample thickness can be obtained using the thermal pulsing technique [16-18]. In this experiment, a non-uniform temperature change, $\Delta T(x,t)$ is established in the sample by shining a short (several μs) pulse of light from a photographic flash gun onto one electrode. During the following few milliseconds, the heat from the absorbed light diffuses through the sample until the temperature is once again uniform. Heat losses from the sample during this period are small.

The electrical response of the sample, i.e., the charge flowing through the external circuit is measured with a wide bandwidth charge amplifier during the thermal equalization period and is recorded by a digital transient recording system for subsequent analysis.

In general, both permanent polarization, $P(x)$, and stored real charge, $\rho(x)$, can contribute to the transient response. The observed signal is a linear combination of the separate effects of charge and polarization. The separation of these two effects is difficult and depends on an understanding of the mechanisms which lead to piezo and pyroelectricity. Fortunately, for many polymers of practical interest, a simplification can be made [17]. If the resistivity, R , of the polymer is sufficiently low, charge migrates through the material in relatively short times. The condition for this to occur is that the Maxwell relaxation time

$$\tau_M = \epsilon \epsilon_0 R \quad (3)$$

be short compared with the time elapsed between poling and the thermal pulse measurement. In Equation (3), ϵ is the relative permittivity of the material and ϵ_0 the permittivity of free space. Such charge motion continues until the electric field in the polymer is zero for short-circuited samples. When this occurs, real charge, $\rho(x)$, and polarization charge, $-dP(x)/dx$, are exactly equal and opposite.

Under these conditions, the transient response equations for the thermal pulsing experiment simplify [17]. It follows that the charge measured under short circuited conditions, $q_{s.c.}(t)$, is given by

$$q_{s.c.}(t) = \frac{\alpha_p C}{\epsilon \epsilon_0} \int_0^d P(x) \Delta T(x,t) dx \quad (4)$$

where α_p is the temperature coefficient of permanent polarization in the material, and C is the sample capacitance.

Two different approaches have been developed for obtaining $P(x)$ both of which assume that one-dimensional heat flow [19] applies during the thermal equilibration process. One method consists of making successive adjustments to a trial distribution until the response calculated from Equation (4) reproduces the experimentally observed transient [16]. The other method determines Fourier coefficients of $P(x)$ from the data using a response equation derived from Equation (4) and the Fourier series form of $\Delta T(x,t)$ [20]. The distributions presented in this paper were obtained by the first method.

Even if no attempt is made to compute $P(x)$, it is possible to make certain statements about the distribution [21]. For example, a uniform distribution results in a step function in the thermal pulsing data. (The front edge of the step is, in fact, slightly rounded due to the finite thermal mass of the metallizing on the heated side. This effect can be calculated accurately.) It is therefore possible to identify the existence of quite small departures from a uniform distribution. In addition, from Equation (4), the ratio of the charge response immediately after the heat pulse ($t=0$) to the charge response at times when the heat is uniformly distributed through the sample ($t \geq \tau$, where τ is the thermal time constant of the sample) yields the ratio of the polarization at the heated side, $P(x=0)$, to the average polarization in the sample, P_{av} , or symbolically,

$$\frac{q_{s.c}(t=0)}{q_{s.c}(t \geq \tau)} = \frac{P(x=0)}{P_{av}} \quad (5)$$

By performing the thermal pulsing experiment from both sides of the sample, it is possible to determine the relative magnitudes of the polarization at either side.

III. RESULTS AND DISCUSSION

The pyroelectric response of PVDF-TFE copolymer to a slowly changing temperature is shown in Figure 1. The measured current is observed to lag behind the rate of change of temperature as evidenced for instance by the displacement between the peaks in i and $\frac{dT}{dt}$. The results also suggest that one cannot in general define a pyroelectric coefficient for these materials which is constant. The pyroelectric coefficient obtained using Equation (1) after both the current and dT/dt became nearly constant is called the "steady-state" pyroelectric coefficient. Values of this quantity as a function of nominal electric field during poling are shown in Figure 2. Repeated measurements on the same film yield a standard deviation of about six percent of the pyroelectric coefficient. The larger deviations apparent in Figure 2 probably arise from additional variations among samples since each data point represents an independent film preparation. Despite the scatter in the data, it is apparent that the level of activity as determined by this method becomes independent of field above about 200 kV/cm and is independent of poling temperatures from 23 °C to 60 °C. This steady state pyroelectric coefficient has been shown also to be essentially independent of poling time over the range 5 minutes to 7 hours [22].

Data from the thermal pulsing technique are presented in Figures 3 and 4 for two films poled at 23 °C and 101 °C respectively. Curve (a) in each case is a recording of the measured charge transient during the thermal equalization time following absorption of a heat pulse on the electrode that was positive during poling. Curve (b) is for a heat pulse incident on the electrode that was negative during poling.

Application of Equation (5) shows that the polarization at the positive electrode is large compared with the average polarization whereas the polarization is small compared to the average at the negative electrode for both poling conditions shown. The polymer poled at higher temperature exhibits a larger average polarization. [Although the ordinates in Figs. 3 and 4 are in arbitrary units, they are approximately the same in the two cases.]

Polarization distributions obtained by successive adjustments to a trial distribution are shown in Figure 5. It is evident that the polarization is concentrated on the side of the positive poling electrode for the sample poled at the lower temperature and extends further into the sample for the sample poled at higher temperature. It also is seen that the polarization is essentially zero on the side of the negative poling electrode in both cases. The above behavior is representative of a general trend for this material over the range of temperature from room temperature to around 100 °C.

The spatial dependence of polarization presumably reflects in some way the spatial variation of electric field in the sample during poling. These results indicate that this field is largest at the positive electrode, decreasing with distance into the material. This will occur only if significant charge exists in the polymer during poling and the spatial dependence of electric field implies that such charge is negative. The charge must arise from the dynamics of the poling process itself since thermal pulsing measurements show that the bulk of the polymer is essentially neutral prior to the start of the poling process.

No definite conclusions can be drawn at this stage about the physical mechanisms which give rise to this charge. Two possibilities are removal of pre-existing charge from the insulator (in which case the mobile charge must be positive) or injection of mobile negative charge into the

insulator. This situation is complicated by the existence of polarization charge in regions of non-uniform polarization which would also contribute to spatial variations in electric field.

The results of Figure 2 (steady-state pyroelectric coefficient essentially independent of poling temperature except for the lowest mean poling fields) and Figure 5 (the fraction of the sample thickness poled increases with the poling temperature) seem to be conflicting since the pyroelectric coefficient measured the mean polarization and an increase in fraction poled implies an increase in mean polarization. The conflict is removed when the difference in time scale of the two measurements is accounted for. It will now be shown that the first measurement, which is made over a period of several minutes, contains a contribution which is only indirectly related to temperature-induced changes in the internal polarization. This contribution to the pyroelectric response is due to slow, reversible motion of real charge through the bulk of the polymer.

This effect can be seen most clearly in the measured charge from a co-polymer following a step temperature change. Note that, on the time scale of this measurement, the temperature at all points in the polymer can be considered essentially uniform. Hence no significant time dependence in the response can be ascribable to temperature gradients, unlike the situation in the thermal pulsing experiment. A typical response from a non-uniformly poled co-polymer is shown in Figure 6(a).

Figure 6(a) shows that the response of a sample to a step temperature change consists of an initial rapid flow of charge, followed by a much slower charge flow in the same direction. The second, slower response takes place over a period of two to three minutes. The rapid response is interpreted as the true pyroelectric effect caused by the change in the average electrostatic polarization within the sample. The slower response is consistent with a model in which real charge migrates through the sample

under the influence of the non-uniform internal electric field generated by the temperature-induced polarization change. This time-dependent charge response is well described by a single exponential time constant of 47s comparable to the Maxwell relaxation time $R\epsilon\epsilon_0$ for the sample indicated by the line nearly coincident with the charge in Figure 6(a). Pyroelectric coefficients obtained from Equation (2) using the charge generated at long times agree closely with the previously mentioned "steady state" values employing a slowly changing temperature and Equation (1).

Figure 6(b) shows the response of a PVDF homopolymer sample to a similar step change in temperature. In this case, only a rapid response component is observed. If any slower response component is present, it must be extremely slow and take place on a time scale much longer than a few minutes. Indeed the Maxwell relaxation time $R\epsilon\epsilon_0$ for the homopolymer sample is at least two orders of magnitude greater than that for the copolymer sample.

Consider the model for a non-uniformly poled polymer shown in Figure (7a). The sample is assumed to be poled to a constant value, P , over part of its thickness ($0 < x < t$) and unpoled over the remainder ($t < x < d$). It is assumed that, after a sufficient period at constant temperature, the polarization charge, at $x = t$, P per unit area, is neutralized by equal and opposite real charge. This reduces the internal electric field to zero. This is not an unreasonable assumption since the Maxwell relaxation time for charge motion within this material, τ_M , is of the order of minutes at room temperature. Indeed, charge motion into the polymer is observed immediately after the completion of poling although this could also be due in part to depolarization effects.

After a few minutes at constant temperature, the polymer therefore contains polarization charge per unit area $+P$ and $-P$ at $x = t$ and $x = 0$, respectively, and real charge per unit area $-P$ and $+P$ at $x = t$ and $x =$

0, respectively. Consider now the effect of a rapid, uniform temperature change, ΔT , in the polymer with the electrodes short circuited. The polarization charge per unit area, P , immediately changes by an amount $\alpha_p P \Delta T$ in accordance with Equation (2). In order to maintain the electrodes at the same potential, real charge of magnitude $\alpha_p P \Delta T (t/d)$ must instantaneously flow in the external circuit from $x=d$ to $x=0$ since the external circuit has essentially zero resistance. Immediately after the temperature change, therefore, the net surface charge densities in the sample are $\pm \alpha_p P \Delta T$ at $x=t$ and $x=0$ (polarization charge), and $\pm \alpha_p P \Delta T (t/d)$ at $x=d$ and $x=0$ (real charge) respectively (Figure 7b). The electric field in the sample is $-\alpha_p P \Delta T (1-t/d)/\epsilon\epsilon_0$ for $0 < x < t$ and $\alpha_p P \Delta T (t/d)/\epsilon\epsilon_0$ for $t < x < d$. This is shown in Figure (7c).

The instantaneous response to a step temperature change is therefore proportional to the average polarization in the polymer. Following this response, however, the electric field in the polymer is non-zero. Real charge therefore begins to move through the bulk of the polymer to reduce this field to zero. Such charge can originate from either electrode, or from within the bulk of the polymer. The experimental results are consistent with a model in which motion of intrinsic charge within the bulk of the polymer is negligible and in which charge injection occurs from the electrode at $x=d$ only.

The possibility of charge injection at $x=0$ is first considered. Two planar charge distributions exist at this electrode--real charge of magnitude $\alpha_p P \Delta T (t/d)$ at the metal-polymer interface, and polarization charge $-\alpha_p P \Delta T$. This latter charge is distributed over a small thickness--perhaps several atomic layers--of the polymer. The situation is illustrated schematically in Figure (7c). Such a charge distribution will give rise to an electric field which reverses in sign a short distance into the polymer as shown. Charges of opposite sign cannot

leave the metal-polymer interface because the field is in the wrong direction. Thus the contact at $x=0$ is blocking for charges of both sign. Charge injection can only occur from the electrode at $x=d$.

Charge which moves through the polymer therefore enters from the unpoled side and moves through the unpoled region $t < x < d$. Such charge motion results in a current in the external circuit in the same direction as that of the instantaneous pyroelectric response $\alpha_p P \Delta T$ (t/d). Charge will continue to flow until the polarization charge at $x=t$, $\alpha_p P \Delta T$, is completely neutralized by real charge. The total charge which flows in the external circuit--instantaneous plus delayed response is therefore equal to $\alpha_p P \Delta T$. This is proportional to the maximum polarization, but independent of the fraction of sample poled.

For a polarization distribution like the one shown in the model of Figure 7, the data shown in the top of Figure 6 yields $t/d = \frac{P_{avg}}{P_{max}} = 0.4$.

The rate at which real charge flows after the temperature change is characterized by the Maxwell relaxation time, $\epsilon \epsilon_0 R$. The resistivity, R , would be expected to increase as the temperature is lowered, causing the delayed response to occur at a slower rate. This is indeed, observed.

The above argument may be shown to be valid for a distribution of polarization which is somewhat more general than the one discussed. It is a straightforward matter to show that a similar response would occur for any distribution which decreases monotonically from one electrode into the polymer. In this case, the instantaneous response is proportional to the average polarization as before. The total charge that flows is proportional to the maximum value of polarization in the polymer.

The measurements of pyroelectric coefficient in Figure 2 which showed near independence of poling conditions can now be explained. When the temperature of the polymer is increased linearly, polarization charge is produced in the bulk of the polymer at a constant rate. This causes a

current flow consisting of two parts--induced charge on the electrodes to maintain them at the same potential and real charge flow into the polymer to neutralize the polarization charge. After a sufficiently long period of constantly increasing temperature, a steady state is reached where the total current flow through the external circuit is equal to the rate of creation of polarization charge. This latter is proportional to the maximum value of polarization, not the average value.

Further confirmation that a non-uniformly poled sample could give rise to a delayed response (manifested by a time dependence of p_y) is obtained from pyroelectric coefficient measurements on bilaminate samples prepared with different polymer films. Figure 8 shows the pyroelectric response from a sample consisting of one layer of unpoled copolymer and one layer of poled PVDF, and for comparison the response of the poled PVDF layer alone. The PVDF homopolymer was capacitor grade material supplied by Kureha Chemical Corporation [14]. It was poled at 800 kV/cm for 30 minutes at 100 °C. It can be seen that the pyroelectric current from the PVDF sample accurately follows the rate of change of temperature. The response of the layered system does not accurately follow the temperature changes--the typically "sluggish" behavior previously noted in partially poled copolymer samples (see Figure 1) is observed but the long-time response (total charge) is the same for equal temperature changes in the two cases.

IV. CONCLUSIONS

A copolymer film of polyvinylidene fluoride and tetrafluorethylene can be made pyroelectric and piezoelectric by the temporary application of high electric fields. For samples poled at fields above 200 kV/cm, the electrical response to slow, linear temperature changes is observed to be essentially independent of poling temperature. Thermal pulsing measurements, however, indicate that such films are only partially

poled. The polarization is significant only near the electrode that was positive during poling and the fraction of the sample that is poled increases with poling temperature.

The pyroelectric response of these non-uniformly poled films to a fast uniform temperature change consists of two parts. The initial, rapid response is proportional to the average polarization in the sample. This is followed by a slower response, which is postulated to be due to flow of real charge into the polymer from the unpoled electrode. This charge neutralizes the temperature induced polarization charge. This model is supported by measurements of the transient response of a layered system consisting of poled PVDF homopolymer and unpoled copolymer.

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FIGURE CAPTIONS

Figure 1. Pyroelectric current i from a VDF-TFE copolymer as the temperature T is decreased over a period of five minutes. The rate of change of temperature is shown as the broken line. The copolymer film was poled for five hours at 60 °C at a field of 300 kV/cm. Electrode area = 4.0 cm².

Figure 2. Steady-state pyroelectric coefficient for a VDF-TFE copolymer film as a function of the electric field applied during poling. Measurements were at room temperature under short circuit conditions. Samples were poled for 35 minutes at poling temperatures of 60 °C(\circ), 25 °C(Δ) and 0 °C(\square).

Figure 3. Charge transfer between electroded surfaces of copolymer film poled at room temperature as a function time following absorption of a heat impulse on one surface of the film. (a) Pulse of heat on the electrode which was positive during poling; (b) heat pulse on negative electrode. Copolymer film is 44 μ m in thickness and poled at 272 kV/cm for 20 minutes at room temperature. The heat pulse was 20 μ s long (FWHM).

Figure 4. Charge transfer between electroded surfaces of copolymer film poled at 101 °C as a function of time following a heat impulse on one surface of the film. (a), (b), as in Figure 3. Poling conditions were 255 kV/cm at 101 °C for 5 minutes. Copolymer film is 47 μ m thick.

Figure 5. Spatial distribution of polarization in copolymer films from Figures 3, 4 for the indicated poling temperatures, T_p . The polarization is largest at the electrode that was positive during poling.

Figure 6. Measured charge transferred between opposing surfaces of polymer film as a function of time following a step-wise change in temperature. (a) Copolymer film poled at 0 °C for 36 minutes at 500 kV/cm, 10 minutes at 600 kV/cm, 10 minutes at 700 kV/cm, 12 minutes at 800 kV/cm and 3 minutes at 900 kV/cm before electrical breakdown. (b) Poly(vinylidene fluoride) homopolymer poled for 30 minutes at 110 °C and 800 kV/cm. Solid line is charge, broken line is temperature; recorder pens are physically off-set. The dashed line nearly coincident with the solid line in (a) represents an exponential curve with a time constant of 47s.

Figure 7. Model for polarization and field within co-polymer. (a) Sample is assumed to be uniformly poled over part of its thickness only. (b) Schematic diagram of uncompensated charges in sample immediately after a temperature change. Circled signs indicate polarization charge. Uncircled signs are real charge. (c) Electric field in polymer due to above charges. (d) Part of (c) near $x=0$ expanded to show field reversal near this electrode.

Figure 8. Pyroelectric current response, temperature, and rate of change of temperature as functions of time. Solid lines refer to a single film of poly(vinylidene fluoride) poled for 30 minutes at 110° C and 800 kV/cm. Broken lines refer to same sample but with a film of unpoled copolymer between the active film and the top contact. Offset of pens in original data has been compensated in this tracing.

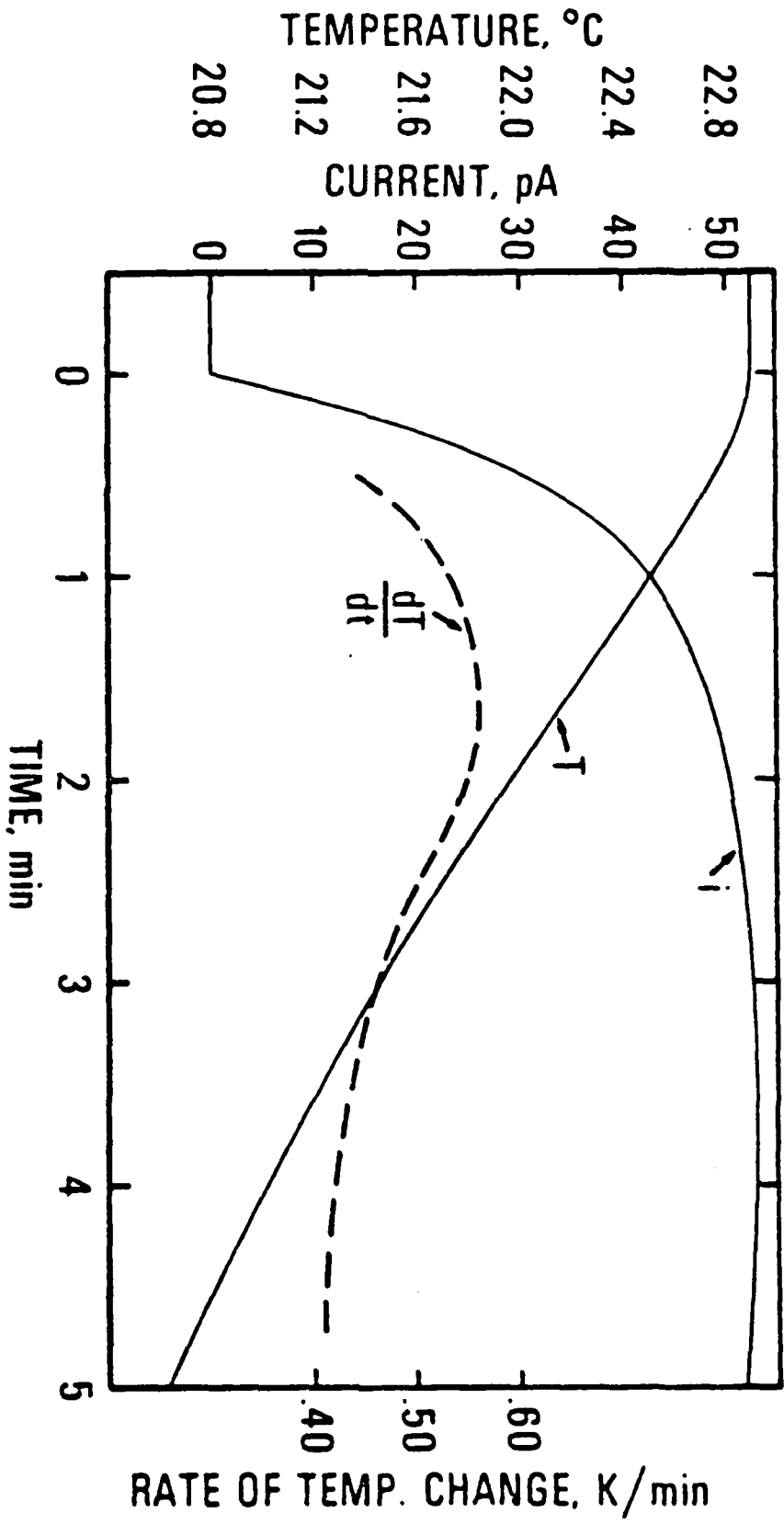


Figure 1

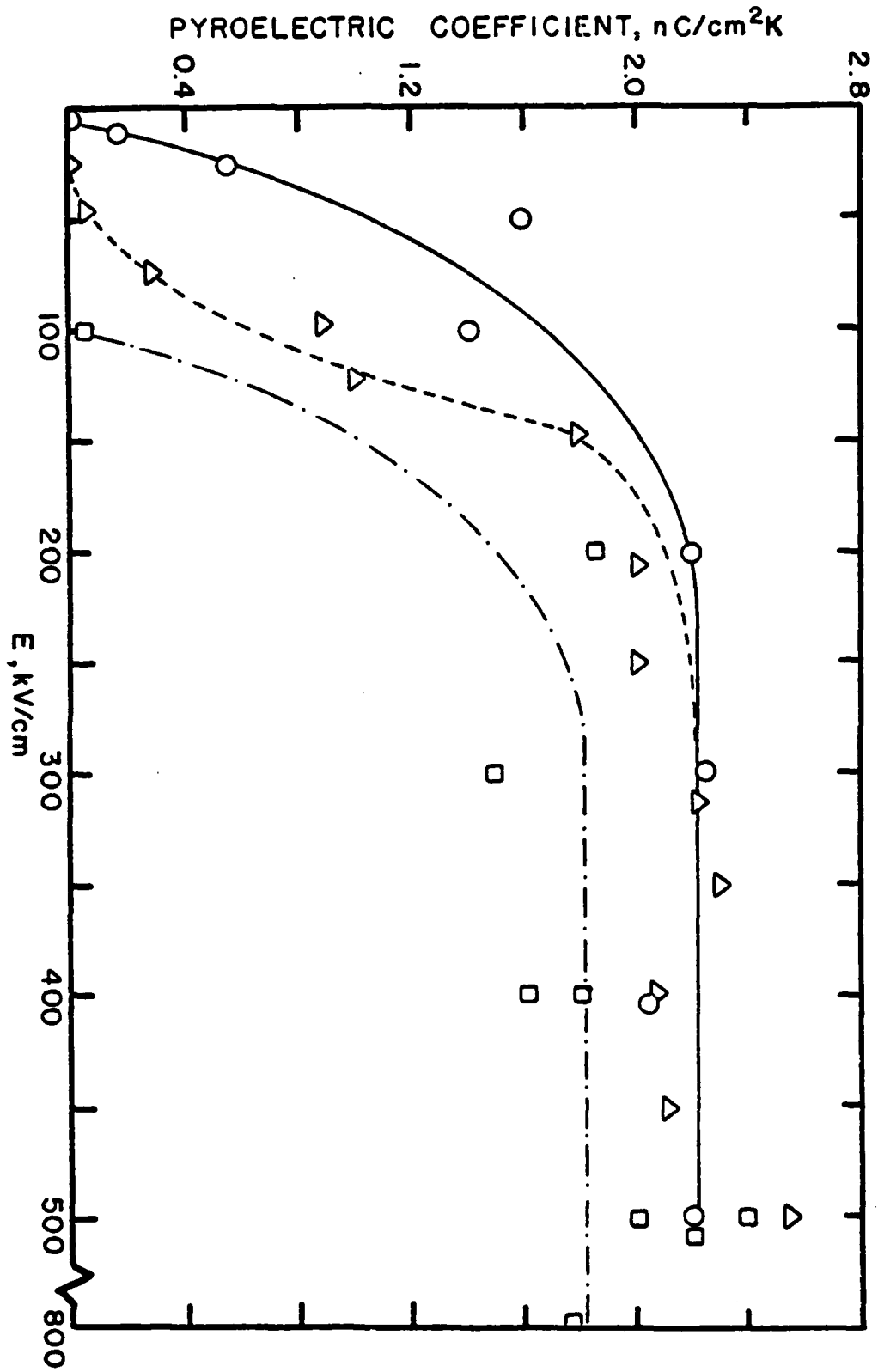


Figure 2

CHARGE, arbitrary units

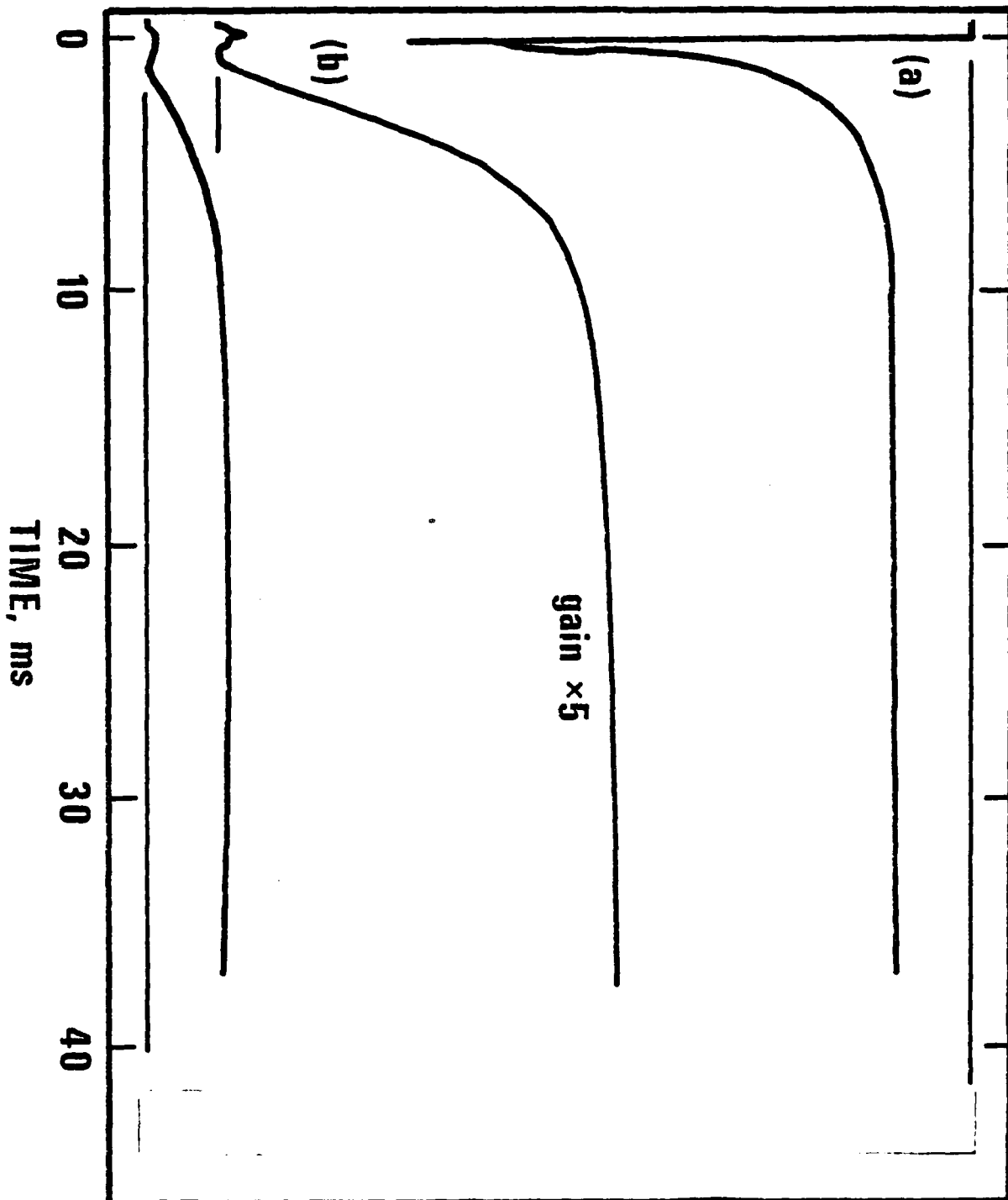


Figure 3

CHARGE, arbitrary units

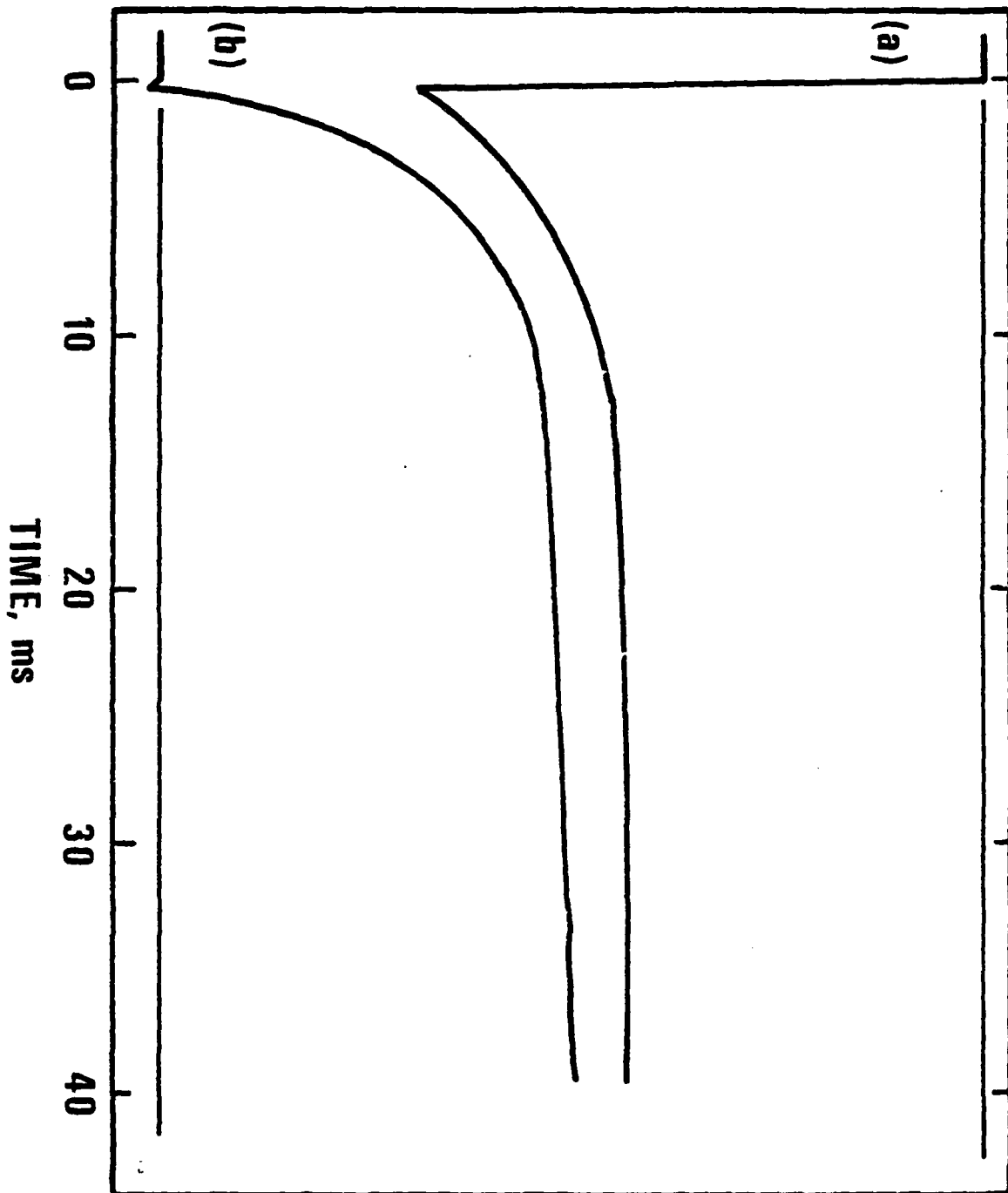


Figure 4

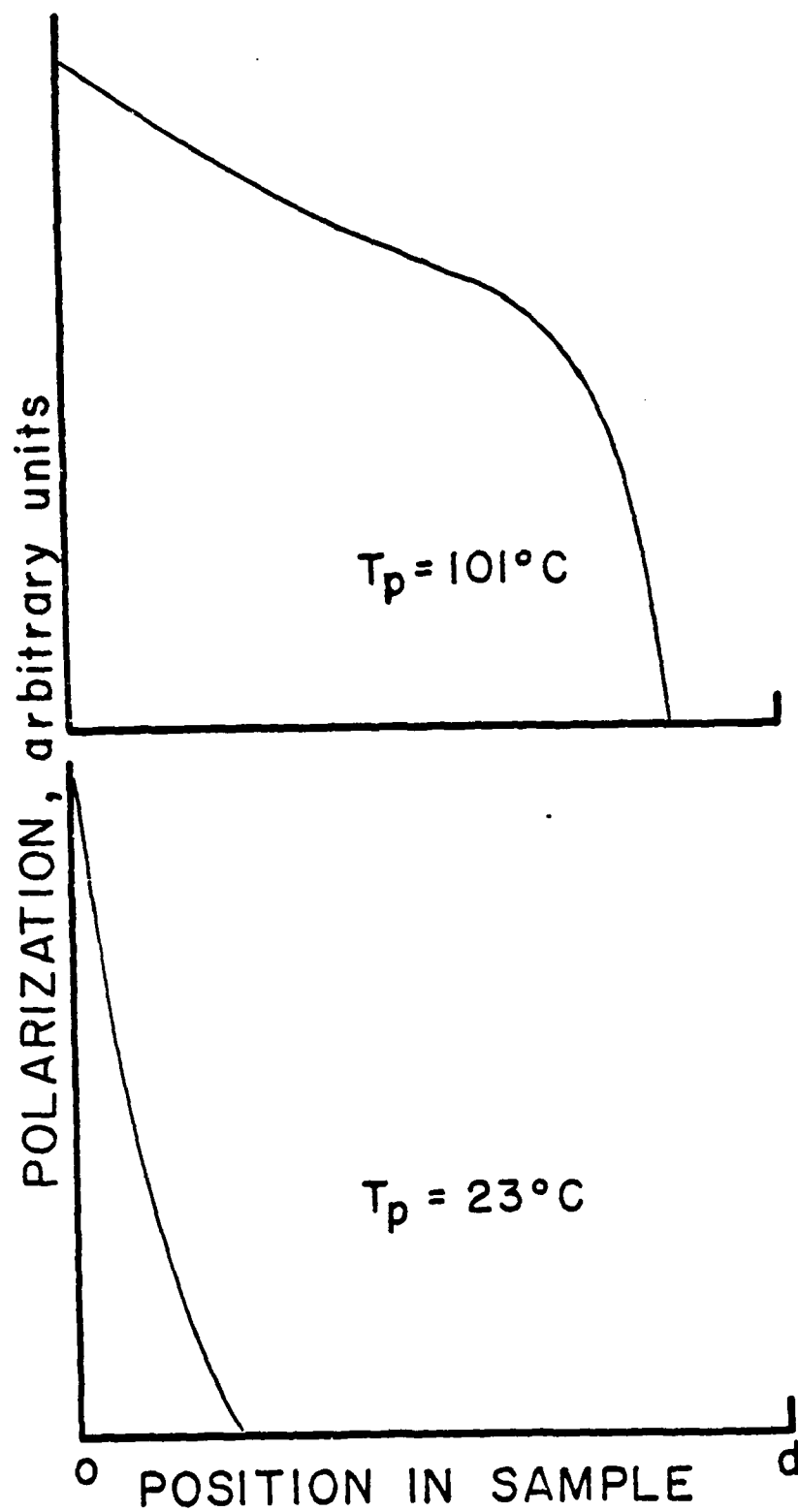


Figure 5

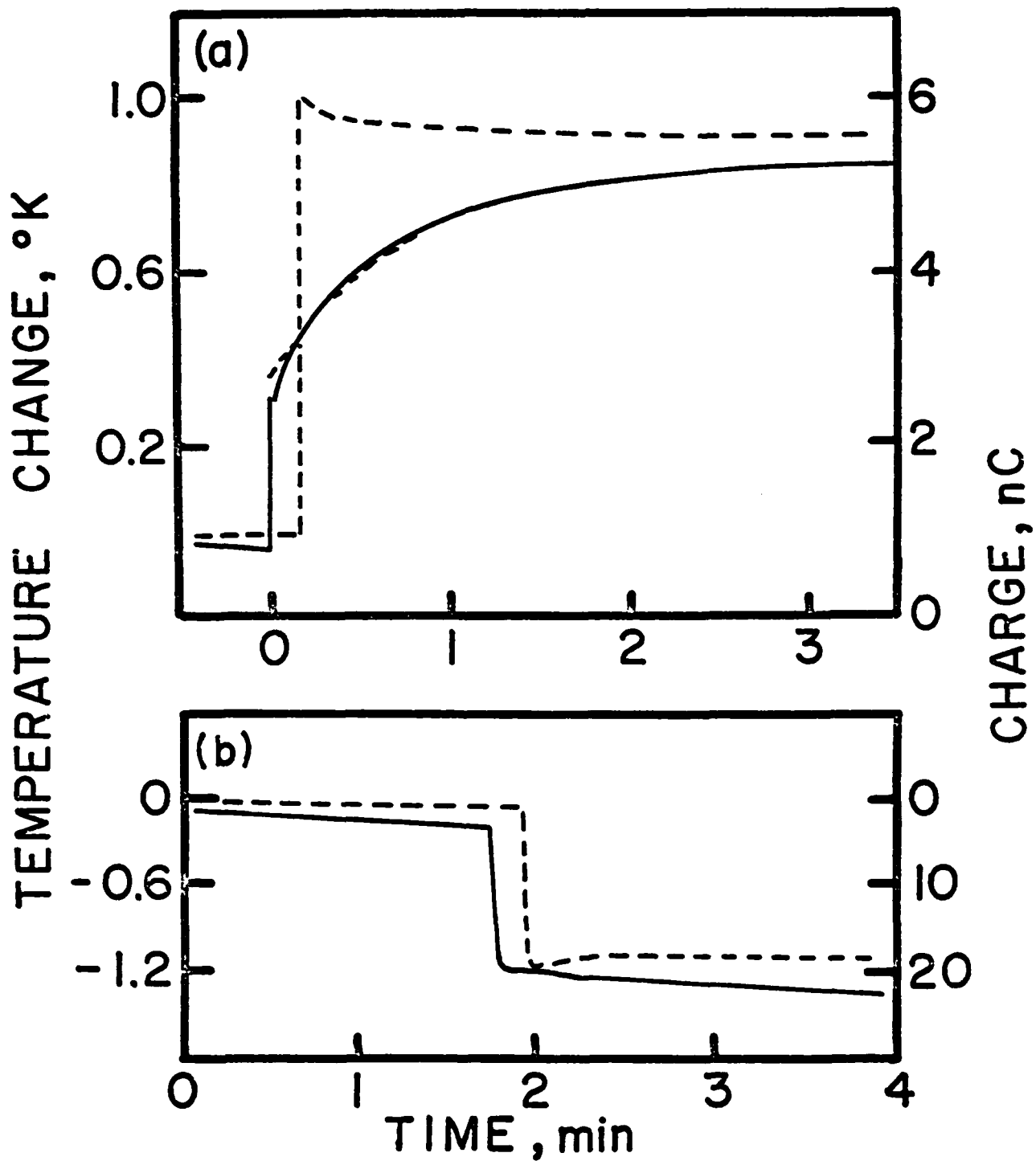


Figure 6

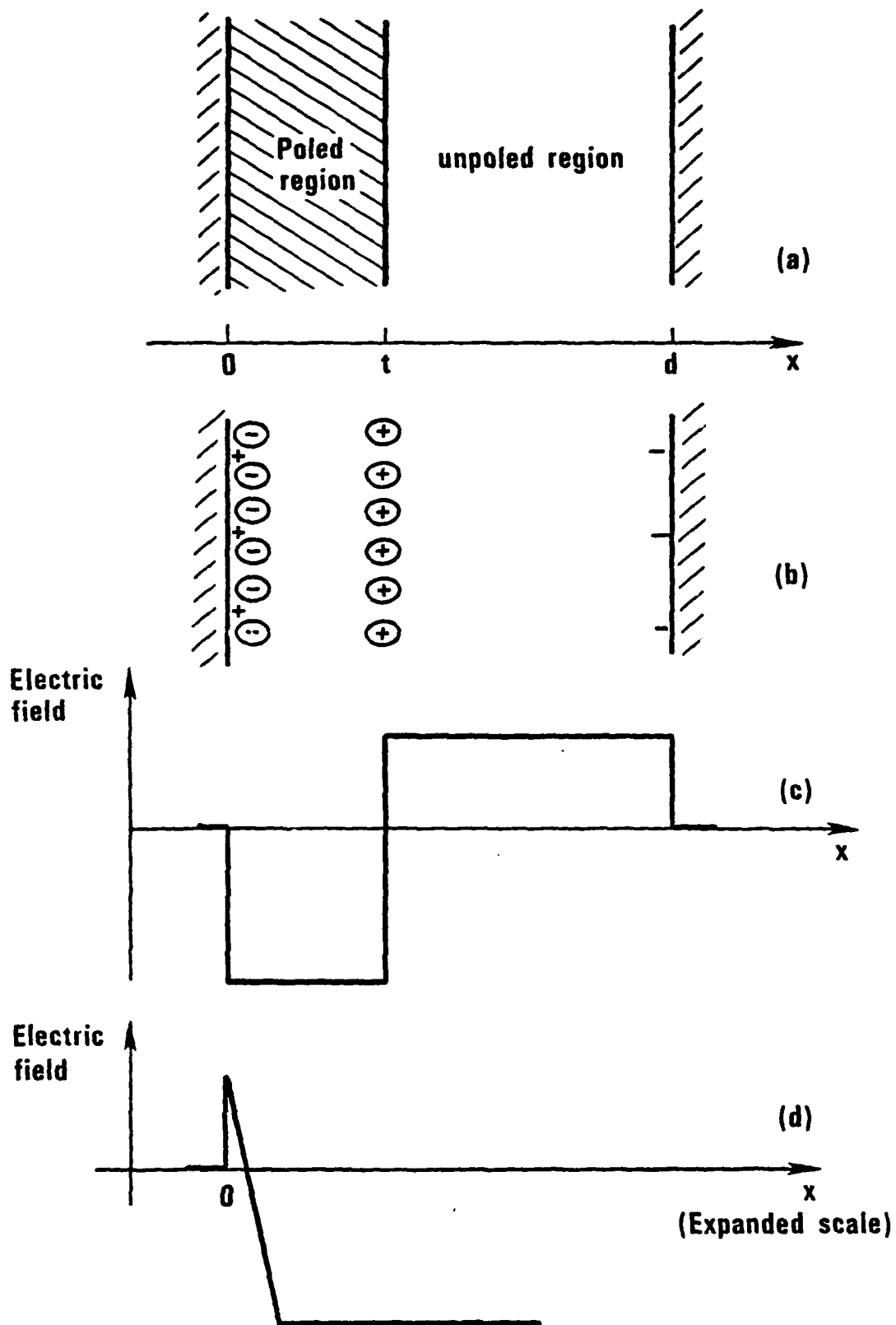


Figure 7

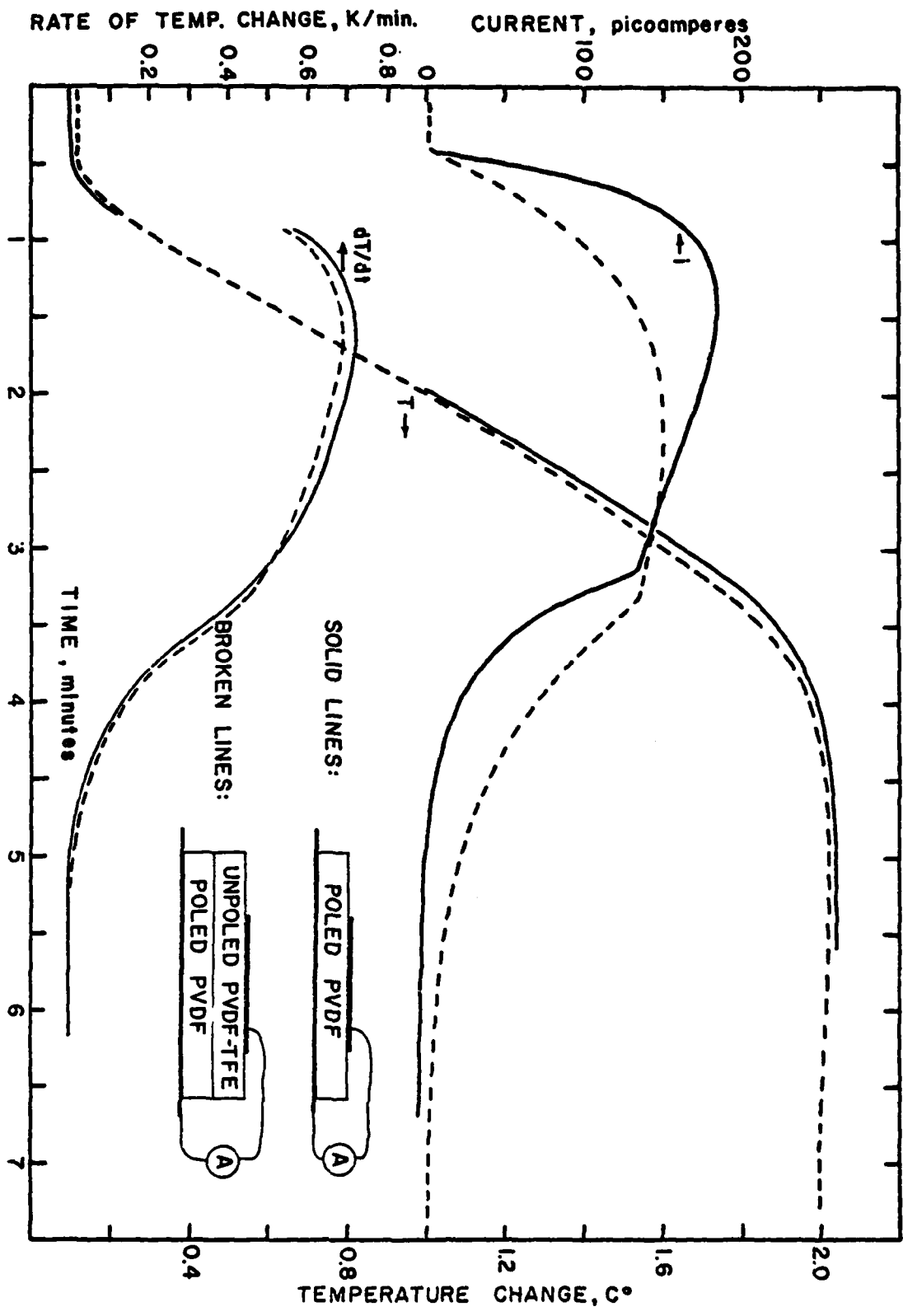


Figure 8

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