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M. G. Broadhurst, G. T. Davis, S. C. Roth
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A copolymer of 73 weight percent vinylidene fluoride and 27 weight percent
tetrafluoroethylene can be made piezoelectric and pyroelectric by the temporary
application of high electric fields. The application of a thermal pulse technique
to the active films reveals that they are polarized preferentially near the posi-
tive electrode and that the polarization extrudes further into the film as the
poling temperature is increased. These observations can be made consistent with
earlier data which show the piezoelectric and pyroelectric coefficient to be

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independent of poling temperature by proposing charge transfer through the unpoled region of the polymer. Transient charge flow following a step-increase in temperature and pyroelectric response from layered structures support this explanation.

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Technical Report

PYROELECTRICITY AND CHARGE TRANSPORT IN A COPOLYMER
OF VINYLIDENE FLUORIDE AND TETRAFLUOROETHYLENE

by

M.G. Broadhurst, G.T. Davis, S.C. Roth, and R.E. Collins

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National Bureau of Standards
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Pyroelectricity and Charge Transport in a Copolymer of Vinylidene Fluoride and Tetrafluoroethylene, M.G. Broadhurst, G.T. Davis and S.C. Roth, NBS, Washington, D.C., 20234, and R.E. Collins, AWA Research Laboratory, North Ryde, NSW, Australia.

I. Introduction

Previous investigations have shown that a copolymer of vinylidene fluoride and tetrafluoroethylene can be made piezoelectric and pyroelectric by the temporary application of an electric field.^{* 1,2} For applied fields in excess of about 250 kV/cm, the electrical response became independent of applied field, independent of poling temperature between 0° and 60°C, and independent of poling time between 5 minutes and 7 hours.^{1,2} Such behavior implied saturation of polarization and values of polarization required to account for the piezoelectric response were well within the maximum to be expected from alignment of dipoles within the crystalline phase of the copolymer. Measurements on similar films now indicate that the polarization distribution within the films is non-uniform and varies with poling temperature. This paper will present these results and will propose a model of charge transfer within the film to reconcile the evidence for saturation polarization and non-uniform charge distribution.

II. Experimental

The copolymer used in this investigation was 73 weight percent vinylidene fluoride and 27 weight percent tetrafluoroethylene supplied to us as a powder by Pennwalt Corporation.³ The powder was evacuated, compressed, and melted in a pellet-making mold commonly used for infrared sample preparation. Small pieces of the pellet were subsequently melted and pressed between Kapton³ polyimide sheets from which the resultant copolymer films were easily removed. Such films were typically 30 to 50 μ m thick

* Literature references have been kept to a minimum appropriate to an extended abstract.

and 3 cm in diameter. When quenched from the melt directly into ice water, the films were 35% crystalline based on density measurements. Aluminum or gold electrodes were evaporated onto both surfaces of the films. The electric field was applied across the sample thickness at room temperature heated to the desired temperature and returned to room temperature before the field was removed.

Since the copolymer crystallizes in a polar crystal form⁴, it can also be poled as it crystallizes from the melt. When crystallized in the presence of an applied field, two different techniques were used to minimize electrical breakdown. When the whole area of the sample was to be poled, a circular disc was cut from a 25 μ m thick polyimide sheet to be used as a spacer between brass electrodes. The copolymer pellet was then pressed into a film filling the void in the insulating Kapton spacer. When only a portion of the film was to be poled, gold electrodes and leads were evaporated onto Kapton sheets between which the copolymer was melted and pressed. The "sandwich" consisting of Kapton sheets and copolymer melt was transferred from the hot press into a copper sleeve immersed in a controlled temperature bath for poling and crystallization. After crystallization, graphite electrodes were painted on the surfaces for electrical measurements.

B. Measurements

The piezoelectric and pyroelectric response was measured as previously described⁵. Briefly, the short circuit current between the electrodes of the sample is measured as the temperature or pressure of the sample is slowly changed. The current per unit area divided by the rate of temperature or pressure change yields the desired coefficients. The pyroelectric response in some cases was also determined by measuring the total charge transferred following a rapid change in temperature. The sample was immersed directly into a stirred beaker of n-hexane and the temperature jump of one or two degrees was accomplished by adding small amounts of chilled or heated hexane.

An indication of the spatial distribution of polarization within the poled samples was obtained using a modification of the thermal pulsing technique reported by Collins^{6,7}. The method relies upon the non-uniform temperature change in a thin film as a heat pulse diffuses through the thickness, d , of the film. Charge generated by the film, $\Delta Q(t)$, can be expressed as a function of the polarization distribution within the film, $P(x)$, and the temperature at any given plane $\Delta T(x,t)$. If the film is initially electrically neutral inside (as would occur for times after poling large compared with the electrical time constant $\epsilon_0 \epsilon' \rho$), it can be shown⁷ that

$$\Delta Q(t) = \frac{C \alpha_p}{\epsilon' \epsilon_0} \int_0^d P(x) \Delta T(x,t) dx \quad (1)$$

In the above expressions, ϵ' , ρ and C are the relative permittivity, resistivity and capacitance of the film respectively and α_p is a temperature coefficient of permanent polarization. Evaluation of α_p depends upon an understanding of the physical processes which lead to the change in polarization; a specific model has been presented elsewhere⁸.

III. Results and Discussion

Figures 1 and 2 show results for two films poled at different temperatures. The charge generated was recorded as a function of time after the absorption of a short heat pulse. In Figures 1 and 2 curves a and b represent the charge generated when the heat pulse is incident on the side that was positive and negative respectively during poling. Curve c is a recording of the change in resistance of the aluminum electrode on the pulsed surface. It is representative of the change in temperature at that surface, and provides a measurement of the thermal time constant of the sample⁶.

It is evident that the charge pulses from the sample are quite different when it is heated from opposite sides, indicating spatial assymetry in the polarization within the film. A quantitative estimate of the spatial distribution of the polarization can be obtained by deconvoluting the data in Figures 1 and 2 using equation (1). The results are shown in Fig. 3. Only the broad features of the distribution are obtained by this technique; fine structure is not resolved.

In the sample poled at room temperature, the polarization is large only very close to that electrode which was positive during poling. Copolymer samples poled at 62, 71, 81, 92, 101 and 106°C also show polarization which is largest near this electrode, and which extends progressively further into the film as poling temperature is increased. Even at the highest poling temperature, however, the polarization is still highly non-uniform.

The spatial dependence of polarization presumably reflects, in some way, the spatial variation of electric field in the sample during poling. We have no convincing explanation of why the electric field in the polymer should be large near the positive electrode and, for lower poling temperatures, essentially zero through most of the polymer. The results suggest a contact dominated process. A possible model may be a reverse-biased p-n junction at the polymer-positive electrode interface with a depletion layer extending into the polymer.

The previous results^{1,2} (pyroelectric coefficient essentially independent of poling temperature) and those of Fig. 3 (different fractions of the sample thickness poled) seemed initially to be conflicting. It can be demonstrated, however, that they are consistent with a model in which real charge migrates through the essentially unpoled region of the sample after a temperature change. This charge moves in the internal electric field produced by the temperature induced change in polarization. Charge motion continues until the internal electric field is zero.

Such a model predicts several features of this transient current. Firstly, the charge motion will take place at a rate dependent on the electrical time constant, $\epsilon_0 \epsilon' \rho$ of the polymer. For PVF₂-TFE copolymer, the resistivity ρ is time dependent, but measurements a few minutes after application of a voltage yield values around 4×10^{13} ohm cm at room temperature. The relative permittivity ϵ' , is frequency dependent and, at 22°C, varies from 9.0 at 100 Hz to 14.2 at 0.01 Hz. The time constant corresponding to these values is about one minute.

This model also predicts the magnitude of the charge transfer for a sample in which the polarization decreases monotonically from one electrode (such as in the present case). The total charge generated (true pyroelectric charge plus the subsequent real charge motion) is proportional to the maximum value of polarization. It does not depend on how far that polarization extends into the sample or on the detailed spatial distribution. In the remainder of this paper evidence is presented which supports this interpretation of the above experimental results.

In order to obtain a more direct indication of the effect, the temperature of some samples was increased in a step-wise manner and the charge transferred was measured as a function of time. The experimental procedure was described above. Results for three different samples are shown in Fig. 4. Co-polymer films poled between 0° and 80°C show a rapid charge flow followed by a time-dependent current of which Fig. 4a is typical. The dotted line in Fig. 4a is an exponential curve with time constant of 0.78 minutes. This is of the order of the electrical time constant discussed above. On the other hand, co-polymer films crystallized in the presence of an electric field, and the homopolymer film, only show the initial rapid response (Fig. 4 b,c). Close examination of the data from the thermal pulsing experiment shows that the charge delivered is still increasing slightly when the temperature in the sample is uniform (Figs. 1, 2). This is also an indication of the beginning of the slow response of Fig. 4a.

To confirm that a non-uniformly poled sample could give just such a response, the pyroelectric response from a layered structure of unpoled copolymer and poled PVF_2 was compared with that from poled PVF_2 alone. PVF_2 homopolymer capacitor grade material supplied by Kureha Chemical Corp.³ was poled at 800 kV/cm for 30 minutes at 110°C. The pyroelectric response is indicated by the solid line in Fig. 5. It can be seen that the pyroelectric current accurately follows the rate of change of temperature. Immediately after obtaining this result, an unpoled copolymer film with electrodes on both sides was inserted between the PVF_2 and the upper contact. The temperature was then changed as before. The results are indicated by the dashed line in Fig. 5. It can be seen that the current response due to a temperature change is not as rapid.

The apparent pyroelectric coefficient for these two cases is shown in Fig. 6 for different times after the commencement of a temperature change. The total charge transferred, obtained by integrating the data of Fig. 5, is found to be similar in both cases yielding a pyroelectric coefficient of $2.45 \text{ nC/cm}^2 \text{ K}$ as indicated by the bar at the right of Fig. 6. It can be concluded that, under the nearly static measuring conditions here, a non-uniformly poled sample can yield the same pyroelectric response as a uniformly poled sample, if there is sufficient conductivity in the unpoled part of the polymer.

IV. Acknowledgement

Partial support of this work by the Office of Naval Research is gratefully acknowledged.

Figure Captions

- Figure 1: Charge transfer between electroded surfaces of copolymer film poled at 23°C as a function of time following absorption of a heat impulse on one surface of the film; (a) when pulsed on the electrode which was positive during poling; (b) heat pulse on negative electrode; (c) resistance change of aluminum electrode which indicates temperature history of pulsed surface. Copolymer film is 44 μm in thickness and was poled at 272 kV/cm for 20 minutes at room temperature. The heat pulse was 20 μs long (FWHM) for the charge measurements and 50 μs long (FWHM) for the resistance trace.
- Figure 2: 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) and (c) as in Fig. 1. Poling conditions were 255 kV/cm at 101°C for five minutes. Copolymer film is 47 μm thick.
- Figure 3: Spatial distribution of polarization in copolymer films from (a) poled at 101°C, (b) poled at 23°C as in Figs. 1 and 2. The polarization is largest at the electrode that was positive during poling.
- Figure 4: Charge transfer between opposing surfaces of polymer film as a function of time following a step-wise change in temperature; (a) copolymer film poled at 0° in a field of 800 kV/cm; (b) copolymer film crystallized in presence of a field of 70 kV/cm; (c) poly(vinylidene fluoride) homopolymer poled for 30 minutes at 110° and 800 kV/cm. Pens for charge and temperature are physically offset.
- Figure 5: Pyroelectric current response and temperature as a function of time. Solid lines refer to a single film of poly(vinylidene fluoride) poled for 30 minutes at 110° 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 6: The apparent pyroelectric coefficient at various points in time from the curve in Fig. 5. Solid circles refer to the single film of homopolymer; open circles refer to the two-layer configuration. The bar at the right corresponds to the coefficient obtained from integration of either curve in Fig. 5. Time axis refers to point of departure of current from zero in Fig. 5.

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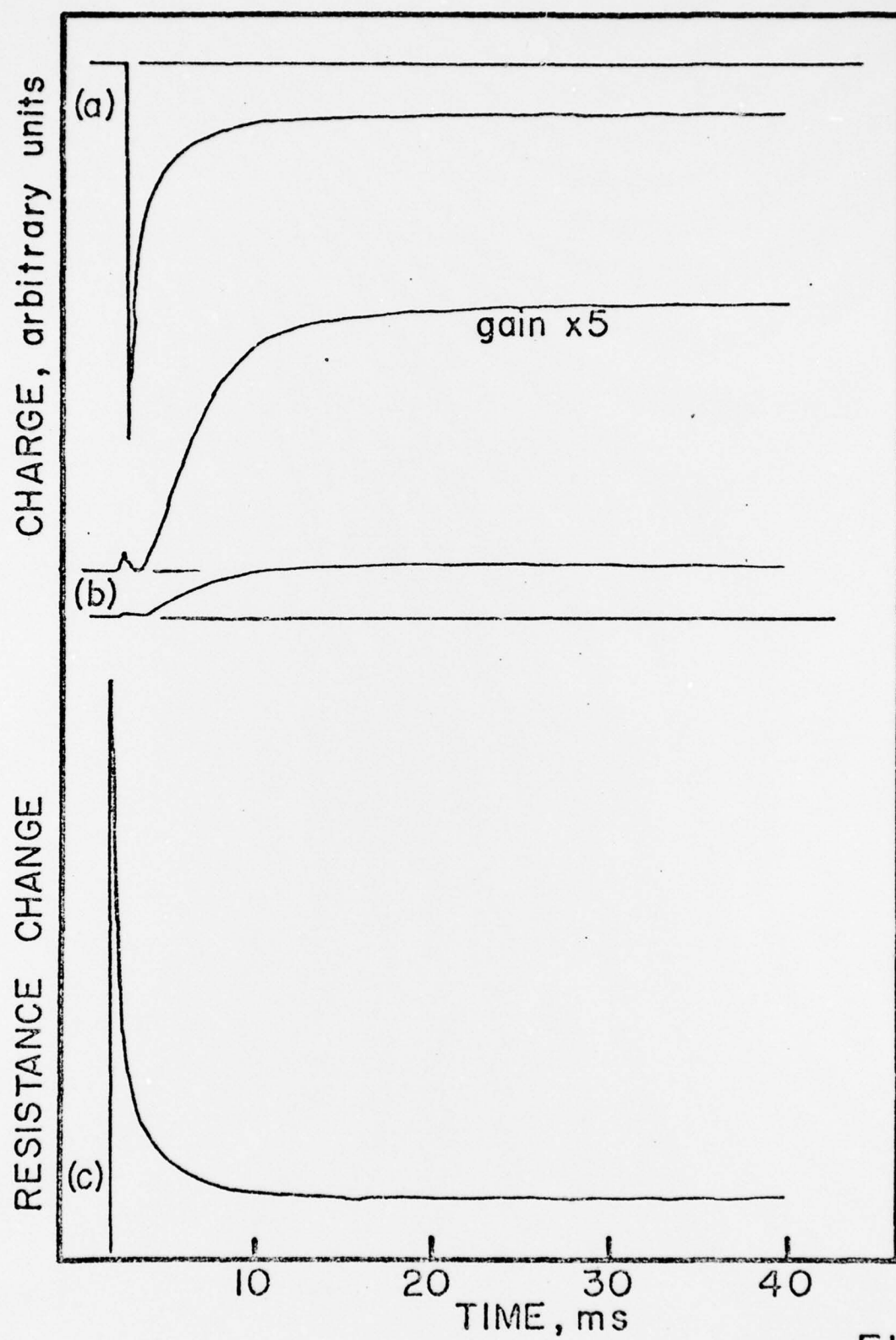


FIG. 1

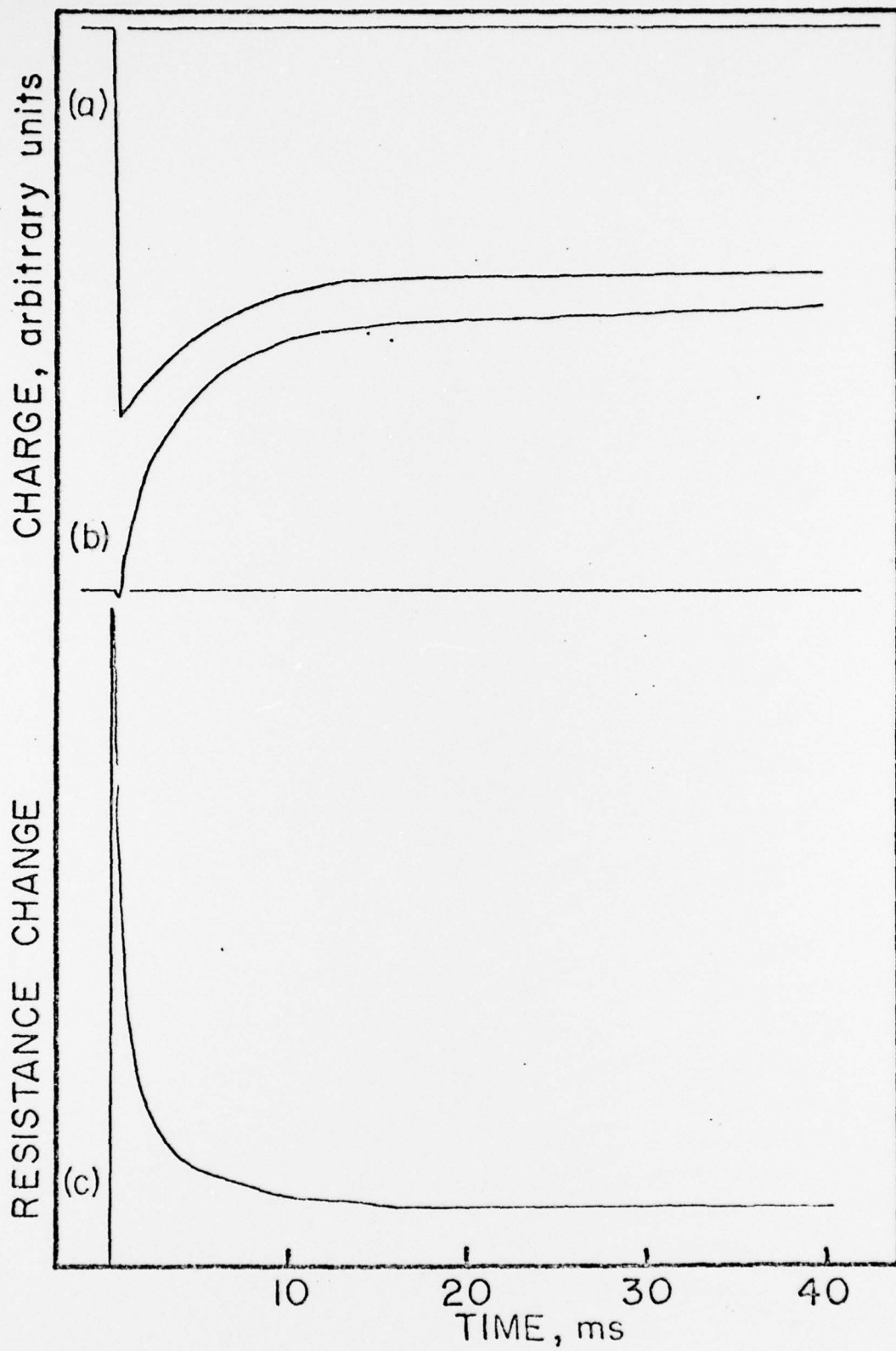


FIG. 2

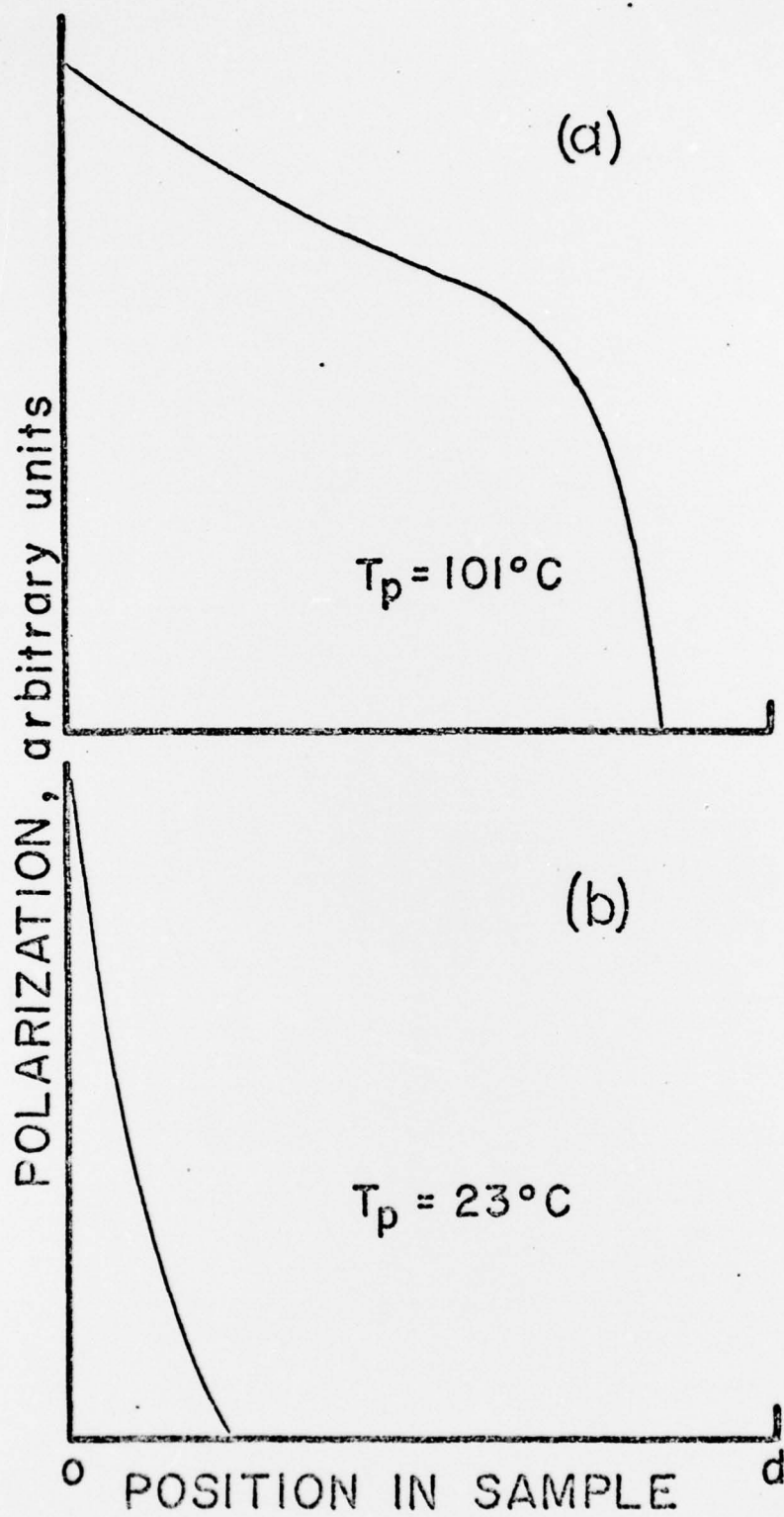


FIG. 3

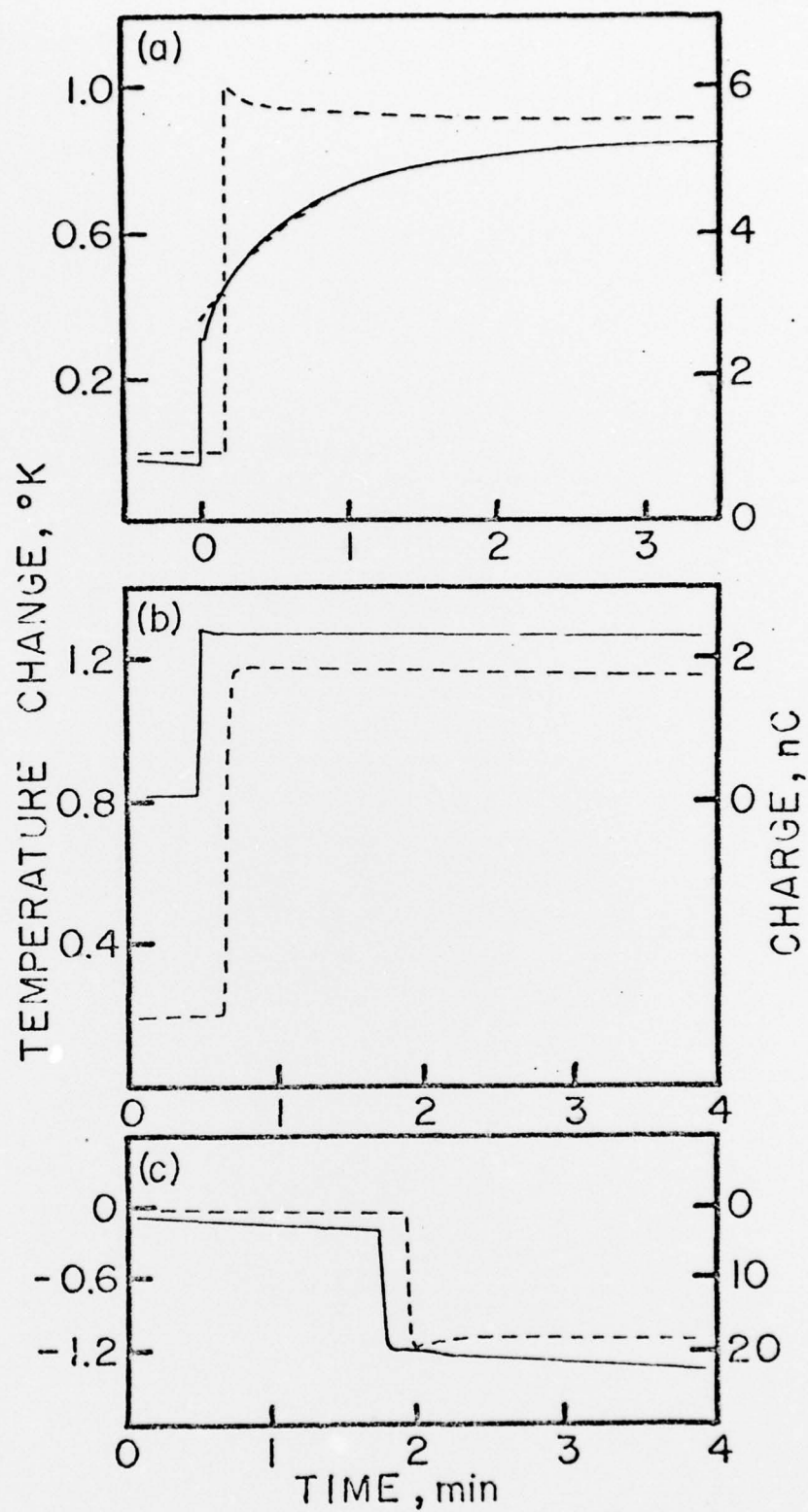


FIG. 4

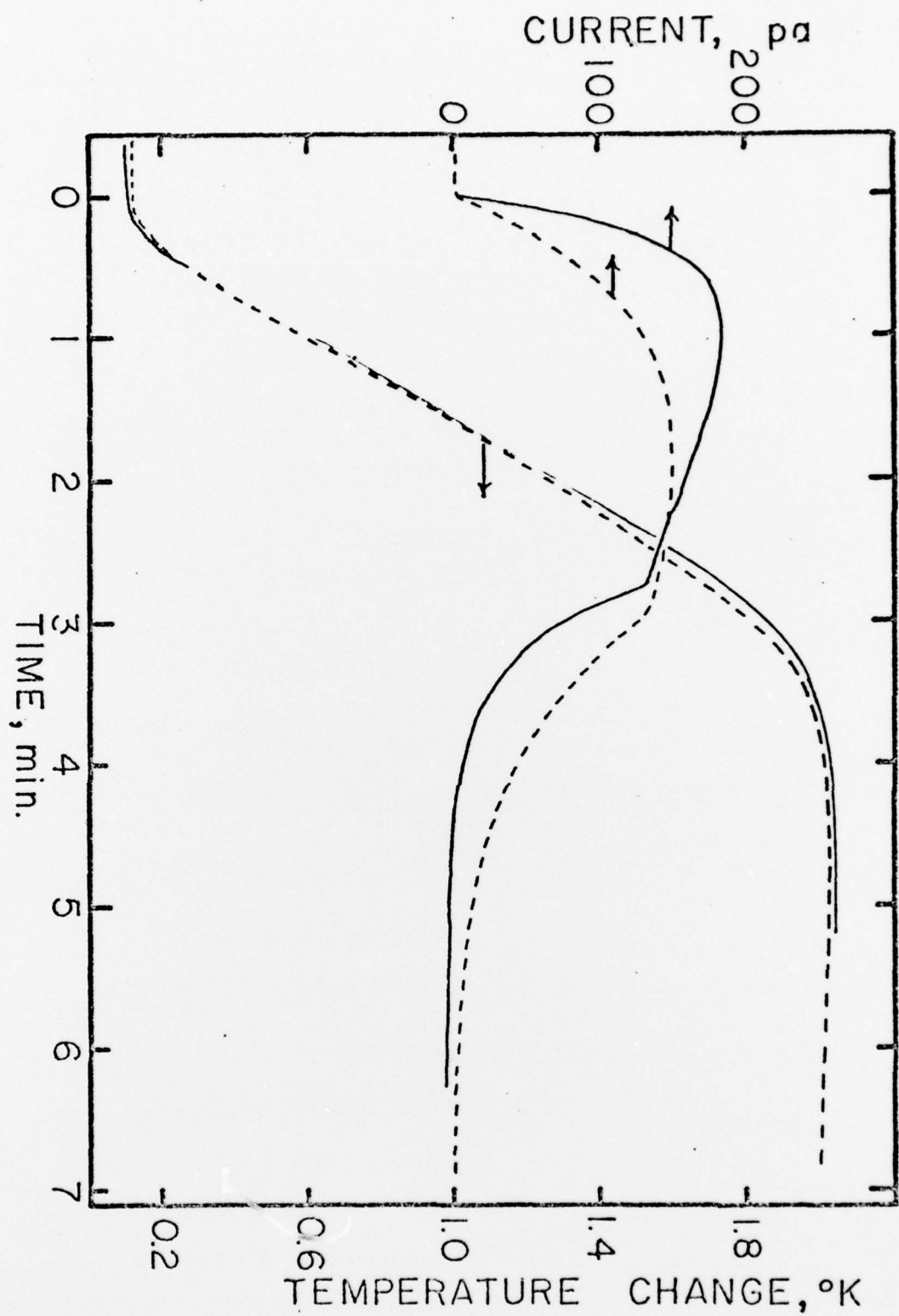


FIG. 5

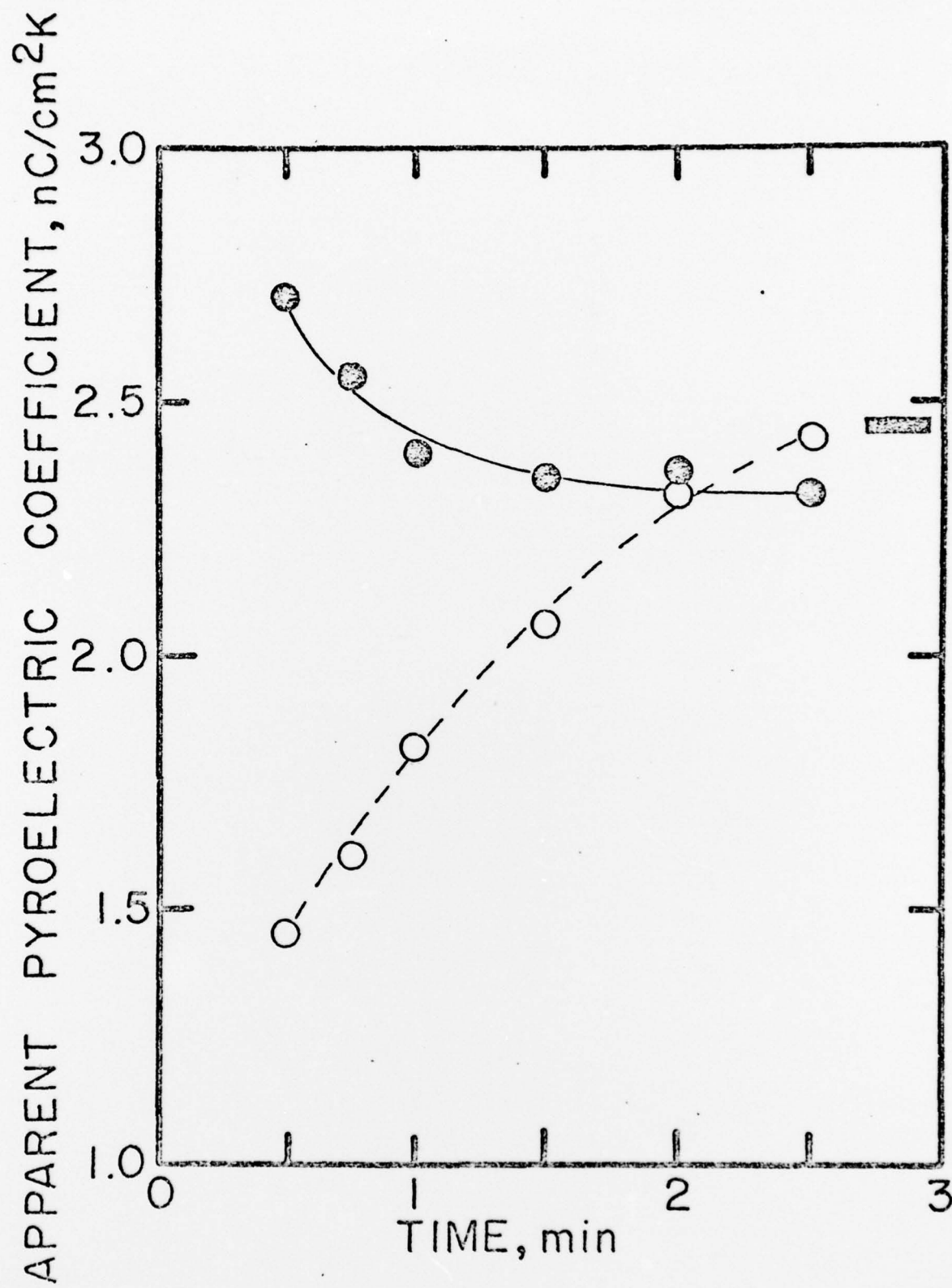


FIG. 6

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