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Abstract

Investigations which should further our understanding of the fundamentals of piezoelectricity in polymers have been carried out using a copolymer of vinylidene fluoride and tetrafluoroethylene. This copolymer crystallizes directly from the melt into a polar crystal form and the crystalline fraction is easily varied from 0.35 to 0.5. Alignment of dipoles in an applied electric field appears to approach saturation at nominal electric fields of 250 kV/cm and is nearly independent of poling temperature between 0° and 80°C. Piezoelectric responses from samples of varying crystallinity are consistent with increased polarization but lower compressibility as the degree of crystallinity is increased.

Thermal pulse experiments which yield information on the charge density distribution across the thickness of the film reveal that the polarization is non-uniform. When poled at room temperature, only a thin region near the positive electrode is poled and the thickness of this region increases with an increase in poling temperature. Charge transport through the unpoled region occurs with a time constant of the order of one minute at room temperature so that thickness of the poled region becomes unimportant in slow measurements.

Copolymer films crystallized from the melt in the presence of a field show greatly improved stability of piezoelectric activity when stored at elevated temperatures compared with samples poled only after crystallization. Furthermore, there are visual differences between the poled and unpoled regions of such a film which have yet to be explained.

The room temperature poling of polyvinylidene fluoride using a corona discharge has been confirmed. Preliminary results are presented which imply that even the non-polar α phase of the polymer may be poled in this way but it is unstable--especially at elevated temperatures.

I. Introduction

The object of the research on the fundamentals of piezoelectricity in polymers is to understand the mechanism responsible for the effect, to enable the selection of polymers with the maximum electrical response and to optimize the conditions for introducing and maintaining the piezoelectric activity. With the aid of ONR funding, previous work in this laboratory has led to an understanding of the piezoelectric and pyroelectric response in amorphous polymers like poly(vinylchloride), in terms of dipole alignment⁽¹⁾. The dipole alignment (volume polarization) is achieved by the application of an electric field at temperatures above the glass transition, T_g , while the polymer is mobile, and the alignment is frozen-in by cooling below T_g before removing the field. Electrical response to a change in pressure is adequately accounted for by the change in volume and the corresponding change in polarization (net dipole moment/unit volume). In the case of a temperature change, in addition to the thermal expansion (or contraction), a contribution to the change in polarization from a change in the amplitude of oscillation of the dipoles, is determined.

In the case of the much more active semicrystalline polymers like poly(vinylidene fluoride) (PVDF) and its copolymers, the mechanism is not yet fully understood. In contrast to amorphous polymers where the polarization is linear with the applied field and can be calculated from the dielectric properties, the polarization in PVDF and its copolymers is non-linear, and is not simply calculable, as in amorphous polymers, from relative permittivity data. The difference in behavior between amorphous and semicrystalline polymers is best illustrated in Figure 1 which compares the pyroelectric coefficient for PVC and a copolymer of vinylidene fluoride and

tetrafluoroethylene (PVDF-TFE) as a function of the electric field applied to form the electret. When the model developed for amorphous polymers is applied to the PVDF-TFE copolymer, the polarization required to account for the piezoelectric response is comparable to values which can be expected to be achieved in the crystalline region of the polymers. However, the pyroelectric response is larger than can be accounted for by reasonable values for the amplitude of oscillation of the dipoles⁽²⁾. In addition, the instability of the amorphous electrets is understood in terms of the randomization of dipoles in the vicinity of T_g but the reason for the decay of piezoelectric activity in the semicrystalline polymers at elevated temperatures is not yet clear.

Much of the effort during the past year has focussed on the PVDF-TFE copolymer in which we have attempted to make direct experimental measurements of dipole alignment in the crystalline regions and have investigated some aspects of stability of the piezoelectric activity, a matter of vital concern to polymer transducer users. The effects of degree of crystallinity have been studied, samples have been poled during crystallization from the melt, and important information on the uniformity of polarization across the thickness of the films has been obtained. Following a report in the literature of useful results, we have also done some preliminary experiments with corona poling.

II. Piezoelectric and Pyroelectric Properties of PVDF-TFE Copolymer

Poly(vinylidene fluoride) can crystallize in three known crystal structures⁽³⁾. It is generally accepted that one of the two polar crystal forms is required to achieve the desirable piezoelectric response⁽⁴⁾. Although the polar crystal

forms can be obtained to some extent by high temperature annealing^(5,6) or crystallization from some solutions⁽⁷⁾ these forms are most conveniently obtained by mechanical orientation⁽⁸⁾. Lando and Doll discovered that when vinylidene fluoride is copolymerized with sufficient quantities of monomers such as tetrafluoroethylene, trifluoroethylene, or vinyl fluoride, the resulting polymer crystallizes from the melt directly into the polar β phase⁽⁹⁾. For several reasons, we have found it convenient to work with a copolymer of 27% tetrafluoroethylene, 73% vinylidene fluoride. The copolymer was supplied by Pennwalt Corp. with the designation Kynar 7200.⁽¹⁰⁾ At the time of acquisition it was a potentially commercial polymer but at the present time it is not made commercially. Since there is only one crystal form, a simple density measurement can be used to calculate the fraction of polar crystal present and since mechanical orientation is not required, the crystallites can be oriented randomly.

The method of measurement of piezoelectric and pyroelectric coefficients commonly employed in our laboratory has been described previously⁽¹¹⁾ but since several references will be made to it in this report it should be helpful to describe it briefly. The film to be measured is placed at the bottom of a copper cell which rests upon a copper block the temperature of which can be changed gradually by flowing either warmed or chilled water through it. Electrical contact is made to the top electrode of the film and the short-circuit current between the top and bottom electrodes is recorded as a function of time as the temperature of the block is altered. Simultaneously, the temperature is recorded as the output from a thermocouple inserted in the wall of the copper cell. The pyroelectric coefficient is then obtained from the ratio of the

current per unit area to the ratio of temperature change at the same point in time. Piezoelectric response is determined by altering the hydrostatic pressure on the sample by allowing helium gas from a cylinder to leak into or out of the cell through a metering valve. The pressure within the cell is recorded as a function of time simultaneously with the current generated. Compared with sinusoidal techniques, the rate of change of both temperature and pressure is rather slow. Typical recorder traces are shown in Figures 2 and 3.

The pyroelectric coefficient determined in the manner just described is shown as a function of the applied poling field for three different poling temperatures in Figure 4. Each data point represents a separate sample preparation involving melting and quenching into ice water. Despite the scatter, it is apparent that for fields in excess of about 200 kV/cm, the polarization (as reflected in the pyroelectric response) becomes independent of poling temperature--even at 0°C.

As mentioned previously, poling this semicrystalline polymer does not require cooling through a glass transition. Our working hypothesis is that dipoles within crystalline regions of the polymer become aligned with the field by rotation about the chain axis defined by the carbon-carbon backbone of the polymers. The crystalline fraction of the polymer can be increased by slower cooling from the melt than was employed for the samples of Figure 4. Results for poling a film which is 43% crystalline are compared with those for a film which is 35% crystalline in Figure 5. In this case, the piezoelectric coefficient is shown as a function of the field applied at room temperature.

According to the model in which the piezoelectric response arises from the change in volume polarization as the film is compressed⁽¹⁾, the piezoelectric coefficient is given by:

$$d_p = \epsilon_\infty \beta_\ell P \quad (1)$$

where d_p = piezoelectric coefficient for an increase in hydrostatic pressure

ϵ_∞ = high frequency limit of relative permittivity of the film

β_ℓ = linear compressibility of the film

P = polarization arising from dipole alignment.

Linear compressibilities of the samples were measured by using three small pieces of the polymer film to separate the plates of a parallel plate capacitor. Hydrostatic pressure was provided by helium gas from a cylinder and the fractional change in capacitance (corrected for permittivity of He) was equated to the fractional change in thickness of the polymer spacers. β_ℓ for quenched films was found to be $2.1 \times 10^{-10} \text{ m}^2/\text{N}$ and for the slowly cooled film $1.1 \times 10^{-10} \text{ m}^2/\text{N}$. From these values of β_ℓ , the measured d_p 's and the assumed $\epsilon_\infty \approx 3$, Eq.(1) was used to calculate the polarization required to account for the results.

This polarization is shown as a function of the applied field in Figure 6. As expected from a model in which polarization resides only in the crystalline region, the more crystalline samples exhibit a larger polarization; the piezo-

electric response is lower due to the smaller compressibility. Since both samples appear to reach saturation, one can compare the "measured" polarization with the maximum to be expected from the model. Allowing for the enhanced polarization arising from the internal field⁽¹⁾, the maximum polarization to be expected can be estimated from:

$$P = \frac{(\epsilon_{\infty} + 2)}{3} \cdot \frac{\mu}{V} \cdot x \cdot \chi \cdot f_{H-T} \cdot \psi \quad (2)$$

where μ = dipole moment of vinylidene fluoride = 2.1D

V = specific volume of copolymer, cm^3 /average monomer unit

x = fraction of vinylidene fluoride in copolymer = .73

χ = fraction of sample which is crystalline

f_{H-T} = fraction of monomer units which add head to tail in polymerization ≈ 0.9

ψ = averaged component of dipoles which contribute to net polarization due to crystallite orientation.

Comparison with the data of Figure 6 is presented in Table I for various assumptions regarding ψ . A value for ψ depends upon the model one chooses for the realigning of dipoles in the electric field. We do not expect to be able to move or rotate entire crystallites in the field at the temperatures employed for poling so that the orientation of the polymer chain axis is assumed fixed at the crystallization step, viz. random. If one assumes rotation about the chain axis from all possible angles to positions where the plane defined by the chain axis and the net dipole is aligned in the direction of the field, $\psi = 2/3$ for random orientation of chain axes. However, if the crystal lattice

imposes the restriction that only 180° rotations are allowed, then only the component of the dipoles that lie in a single direction will contribute to the net P and $\psi = 1/3$. From the agreement in Table I, it appears that $\psi = 1/3$ which has important implications regarding the ability to detect changes in dipole alignment as will be discussed in the following section.

III. Attempts to Measure Dipole Re-Orientation

A. Models

Figure 7 shows a schematic representation of folded-chain polymer crystallites as they are thought to exist in a semi-crystalline polymer. The parallel lines represent a sequence of covalently bonded carbon atoms which form the "backbone" of the polymer chain commonly referred to as the chain axis. Small arrows indicate the dipoles of the (CH_2CF_2) repeating monomer units in the chain which are normal to the chain axis in the polar crystal form. Large arrows emphasize the net dipole of the crystallite--meant to be oriented at random in the unpoled polymers on the left. In general, polymer crystallites are 10 to 40 nm thick (the dimension depicted in the figure) and on the order of $1 \mu\text{m}$ in lateral extent. For simplicity, only crystallites with the chain axis parallel to the plane of the paper are considered in Figure 7 for now. Because of the restriction to movement of the crystallites imposed by polymer molecules which probably exist as tie-chains between crystallites and the very high viscosity of the surrounding non-crystalline regions, the crystallites are not expected to move significantly in the poling process. One can, however, envision realignment of dipoles in the electric field through rotation about the chain axis within the crystal lattice similar to the motion proposed for the crystal relaxation in polyethylene which occurs above room temperature⁽¹²⁾. A crystal relaxation has been observed in PVDF in the anti-polar α form⁽¹³⁾ and in the polar crystal of poly(vinylfluoride)⁽¹⁴⁾ but as yet, experimental evidence for a crystal

relaxation in the β form of PVDF is lacking. The effect of chain axis orientation is best illustrated by the two lowest crystallites in Figure 7. When the chain axis is normal to the film surface across which the poling field is applied as in "A" there will be no contribution to a change in polarization because dipole alignment with the field would require a change in chain axis orientations. However, when the chains are parallel to the surface as in "B", rotation of the molecule about the chain axis could result in aligning the dipole with the applied field and thus contribute to the polarization. In general, the component of the chain axis which lies in a plane parallel to the surface would be expected to contribute as indicated in Figure 7 by the angle δ . Further consideration must be given to the details of such a reorientation by rotation about the chain axis. Lacking from Figure 7 were representations of crystallites with a component of the chain axis normal to the plane of the paper which are considered in Figure 8.

Assuming that rotation about the chain axis is possible, the resulting polarization still depends upon what angular changes can occur. If rotation through all angles is allowed such that the maximum polarization consistent with no change in chain axis occurs, the situation represented by Figure 8(b) would obtain. In this case rotation about the chain axis would have to be accompanied by or followed by translation of the chains with respect to each other in order to re-establish the stable crystal structure. The relative positions after rotation but before translation are shown by the dotted arrows in Figure 8(b). It is this model which leads to $\psi = 2/3$ in Eq.(2). Note that the number of crystallites in a favorable position to diffract x-rays from, say, the 020 planes for a given angle of incidence will have changed in this case.

If rotations of 180° only were allowed such that the relative positions of the chain axes remain unchanged, the situation depicted in Figure 8(c) would be expected. In such a case, the maximum polarization to be expected would depend upon the averaged component of the dipoles in a single direction--the direction

of the applied field. If the dipoles in a randomly oriented specimen are resolved into components directed along the axes of a rectangular coordinate system, $1/3$ of the summed components will lie in a particular direction and $\psi = 1/3$ in Eq.(2). In this model, polarization is achieved by aligning one component of all the dipoles in the same direction but no change in orientation of crystal planes would be detected after poling. Likewise, there would be no change detected in the polarized IR spectrum. As mentioned in the previous section, it is this model which appears to agree most closely with data obtained on the copolymer samples of differing crystallinities. Stronger conclusions should not be reached because of the uncertain applicability of Eq.(1) to the crystalline polymers and the experimental uncertainty in β_{λ} .

Even though no changes in the orientation of crystal planes nor the intensity of polarized IR and Raman spectra as a result of poling would be expected based on the above results, other authors^(15,16,17) have reported such changes. We have also looked for such changes in the copolymer system.

B. X-Ray Scans

The intensity of diffracted x-rays from a set of crystal planes is a maximum when the Bragg condition is met, viz., $n\lambda = 2d \sin \theta$ where λ is the wavelength of x-rays, d is the interplanar spacing, n is the order of the reflection and θ is the angle between the incident beam and the crystal plane. If the angle between incident and diffracted beam is set to correspond to a particular d spacing, say 020, then the 020 planes that are in the right position (inclined at θ degrees to the incident beam) will contribute to the diffracted intensity. Information on the orientation of crystal planes within a sample can be obtained by recording the diffracted intensity at fixed θ positions as the sample is continuously repositioned in the x-ray beam. Such data obtained for a series

of different d-spacings are known as x-ray pole figures⁽¹⁸⁾. Preliminary to such extensive measurements before and after poling, we looked for changes in intensity of diffraction from crystal planes of different spacings with the copolymer film in a fixed position as the voltage across a 50 μm thick film was increased in steps of 500 V to 2000 V. Successive seams were superimposable, indicative of no change in orientation.

C. Raman Spectroscopy

Preliminary measurements have been made using Raman spectroscopy to detect changes in dipole alignment. A purposely thick film (100 μm) was prepared by slow cooling from the melt and plated with evaporated gold electrodes. The film was cut and illuminated on the edge. The incident beam passed through a small hole in a mirror at 45° to the direction of propagation and was polarized in a direction normal to the surface of the film. Back scattered radiation was reflected from the mirror into the collecting system through a polarizer whose direction was parallel to the surface of the film. Near the end of one scan the region of the sample being illuminated was burned out by the laser beam. Upon repositioning the sample, a spectrum with a vastly different distribution of intensities was obtained as shown in Figure 9. Inhomogeneities on the scale of the laser beam (ca. 40 μm diam) require then that the effect of poling must be investigated by repeating measurements on exactly the same region of sample. When 500 volts was applied across the film (50 kV/cm) at room temperature there was an increase in background intensity due to fluorescence but no detectable change in the spectrum in the region from 750 to 900 cm^{-1} . Upon applying 1000 volts, breakdown between the high voltage electrode and a grounded portion of the apparatus occurred and the experiment has been discontinued for the present.

D. Optical Microscopy

An attempt was also made to observe changes in the optical extinction pattern of a cross section of copolymer film between crossed Nicols as an electric field was applied at room temperature. No changes were observed but the experimental arrangement may be of interest for further work. A thin film of copolymer which had been oriented by rolling was coated with evaporated aluminum electrodes about 1000 Å thick on each side. Teflon tubing about 4 mm I.D. was cut in two lengthwise, the film placed between the halves of tubing and then held together by inserting in Tygon tubing of appropriate I.D. Molten Woods metal was poured into this mold so as to create a semi-circular contact on each side of the copolymer film. The film with the adhering Woods metal was then cast in epoxy and 25 µm-thick slices were cut on a microtome. Finally, electrical leads were connected to the Woods metal portion of each slice using silver-filled epoxy. A sketch of the resultant cross-section is presented in Figure 10. Electrical breakdown occurred at about 700 volts in several samples.

In view of the tentative conclusion of only 180° rotation of dipoles mentioned in section IIA and the incomplete poling at room temperature to be discussed in the following section, the absence of observed changes in x-ray, Raman and optical microscopy is not surprising. Discrepancies between these results and the reports of others^(15,16,17) have yet to be explained.

IV. Thermal Pulse Experiments

Dr. R. E. Collins of AWA Research Laboratory, North Ryde, Australia worked in our laboratories for about seven weeks in early 1976 during which time he set up an apparatus for measuring charge distribution in polymer films similar to the one he previously described⁽¹⁹⁾. Briefly, the method relies upon the thermal expansion and subsequent contraction of different regions of the film with their associated charge and concomitant polarization changes as a heat pulse diffuses through the thickness of the film. If the polarization charge

is cancelled throughout the film by real charge, then the charge per unit area $\Delta Q(t)/A$ generated at the metal electrodes as a result of the thermal pulse can be expressed as a function of the polarization distribution within the film, $P(x)$ and the temperature increase at any given plane $\Delta T(x,t)$ (19)

$$\frac{\Delta Q(t)}{A} = \frac{\alpha_p}{d} \int_0^d P(x) \Delta T(x,t) dx + \frac{(\alpha_p + \alpha_x - \alpha_\epsilon)}{P(d)} P(d) \Delta T_{eq} \quad (3)$$

in which A is the area of the pulsed electrode, α_p , α_x and α_ϵ are the thermal coefficients [e.g. $\frac{1}{P} \left(\frac{dP}{dT}\right)$] of polarization, P , thickness, x , and relative permittivity, ϵ , respectively. The distance from the pulsed electrode to an arbitrary plane in the film is x and the total thickness is d , $P(d)$ is the polarization at $x = d$ and ΔT_{eq} is the temperature change when the temperature

Figures 11 and 12 show results of Collins 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 11, and 12, 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 measurement of the thermal time constant of the sample (20).

It is evident that the charge pulses from the sample when heated from opposite sides are quite different, 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 11, and 12 using Eq.(3) which has been done by Collins. The results are shown in Figure 13. 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 the higher the poling temperature. Even at the highest poling temperature, however, the polarization is still highly non-uniform. However, poly(vinylidene fluoride) homopolymer poled at 100°C at fields near 800 kV/cm exhibit nearly uniform polarization by this technique.

The spatial dependence of polarization presumably reflects in some way the spatial variation of electric field in the sample during poling. This non-uniform field is associated with non-uniform space charges in the specimen during poling, but we have no detailed description of the space charge behavior as a function of time and temperature. The assumption of negative charge injection at the negative electrode and mobility of the charges through the bulk is one possible explanation of the effects.

The results shown in Figure 4 (pyroelectric coefficient essentially independent of poling temperature) and those of Figure 13 (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.

In such a model, 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.

The 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 the polarization extends into the sample or on the detailed spatial distribution. In the remainder of this section 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. Poled polymer films were immersed in a stirred beaker of hexane and the temperature was changed rapidly stepwise by adding small amounts of heated or cooled hexane. The temperature changes of about 2°C were measured with a thermocouple and the charge transferred from one surface to the other was converted to a voltage using an operational amplifier. Co-polymer films poled between 0° and 80°C show a rapid charge flow followed by a time-dependent current of which Figure 14a is typical. The dashed line fitted to the solid curve in Figure 14a 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, the homopolymer film, (PVDF) which appears to be uniformly poled from the thermal pulse experiments shows only the initial rapid response as

shown in Figure 14b. 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 (Figures 11 and 12). This is also an indication of the beginning of the slow response of Figure 14a.

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 PVDF was compared with that from poled PVDF alone. PVDF homopolymer capacitor grade material supplied by Kureha Chemical Corp.⁽¹⁰⁾ was poled at 800 kV/cm for 30 minutes at 110°C. The pyroelectric response is indicated by the solid line in Figure 15. 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 PVDF and the upper contact. The temperature was then changed as before. The results are indicated by the dashed line in Figure 15. 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 Figure 16 for different times after the commencement of a temperature change. The total charge transferred, obtained by integrating the data of Figure 15 is found to be similar in both cases yielding a pyroelectric coefficient of 2.45 nC/cm²K as indicated by the bar at the right of Figure 16. 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.

V. Crystallization in an Applied Field

As mentioned previously, it seems very unlikely that crystallites in the semicrystalline polymer can be rotated by the applied field. However, if poled as the polymer is cooled slowly from the melt it may be possible to orient newly formed crystals in the field before they become entangled with neighboring crystallites. Since the copolymer crystallizes in the desired polar crystal form without mechanical deformation, it is possible to attempt this poling during crystallization. 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 μm thick Kapton⁽¹⁰⁾ 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⁽¹⁰⁾ spacer. When only a portion of the film was to be poled, gold electrodes and leads were evaporated onto Kapton⁽¹⁰⁾ sheets between which the copolymer was melted and pressed. The "sandwich" consisting of Kapton sheets and copolymer melt was transferred from the hot press to 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.

It has been possible to pole the copolymer as it crystallizes. Dilatometric measurements indicate that crystallization starts around 119°C but at these temperatures the maximum field that we have been able to apply without breakdown has been about 80 kV/cm. Consequently, the piezoelectric response is not as large as achieved for samples poled at higher fields but the resulting properties

are extremely interesting. The most encouraging aspects of such experiments are that the resulting piezoelectric activity is stable at elevated temperatures and one can visually distinguish the poled region from the surrounding unpoled regions.

Although the copolymer can be poled at room temperature to what appears to be saturation, the activity decays with time. Typical data at a series of temperatures are shown in Fig. 17. In contrast, the samples poled during crystallization show very little decrease with time, even when stored at 100°C. The data are shown for storage temperatures of 60, 80, and 100°C in Fig. 18. Although the response is not as large initially, the stability of such samples means that there is nothing intrinsically unstable about the polarization in a copolymer of this composition.

Another interesting result of poling during crystallization is that one can visually distinguish a difference between the poled and unpoled region but so far we have not found any instrumental technique that will help to explain the difference. The photograph in Fig. 19 is of a copolymer film crystallized between Kapton⁽¹⁰⁾ sheets with evaporated electrodes. The grounded electrode was split so that only one-half of the sample was subjected to the field but both halves crystallized under the same conditions otherwise, including the presence of gold on both sides. The picture was taken with the film between crossed polaroids. In a density gradient column, a portion from the poled side exhibited a density of 1.885 g/cm³ vs 1.887 g/cm³ from the unpoled region but further measurements must be made to be confident of differences of this magnitude. The infra red spectra are essentially identical; fourier transform IR were taken at

several positions on each side and the difference spectrum indicates no variation between positions. There may, however, be a measurable difference in the x-ray diffractometer scans. In Fig. 20 are shown tracings of diffractometer scans from the two halves of a similar sample. The peak in the vicinity of $20^\circ 2\theta$ is shifted by about 0.2° toward higher angles in the poled portion of the film. Unfortunately, no internal standard was run to insure that both halves were properly aligned on the diffractometer stage but such experiments are planned. Quantitative information is difficult to extract from such data because of the near coincidence of several reflections, the relative random crystal orientation and the diffuseness of the peaks exhibited by the copolymer. The reflections which contribute to the intensities of each peak are indicated on the Figure.

One attempt was made to pole the PVDF homopolymer during crystallization using the method described above. K-F⁽¹⁰⁾ film supplied by Kureha Chemical Corporation was subjected to a field of 43 kV/cm at 179°C and cooled to 140°C over a period of 2.5 hours then quenched to room temperature before removing the field. The resulting film was difficult to separate from the Kapton sheets but portions large enough for an IR spectra were obtained from each side (poled and unpoled). Both regions of the film exhibited mostly non-polar α -form crystals with no difference in relative amount of α and β as evidenced by IR bands at 510 and 530 cm^{-1} .

VI. Corona Poling

A recent report by Southgate⁽²¹⁾ shows that PVDF homopolymer can be poled at all temperatures above -40°C (the usually accepted T_g) using a corona discharge. Furthermore, significant changes in the IR spectra were reported which indicated a conversion from α to β phase upon annealing and subsequent to the corona charging. We have performed some preliminary experiments which confirm that

PVDF can be poled in this way at room temperature. In addition, very interesting results are obtained from different samples. In the experiments performed here, ions in the air above the polymer film were created by discharging a Tesla coil to ground. Only the bottom surface of each film was electroded with aluminum and a negative potential of 3000 volts was applied to the bottom electrode during the discharge. Following the discharge, a graphite electrode was painted onto the top surface to facilitate measurement of the pyroelectric response. IR and x-ray scans were made at each stage by removing the electrodes and then replacing them again (with graphite electrodes). The results obtained for three different films before and after annealing for one hour at 100°C are shown in Table II. The surprising result is that the PVDF in the non-polar α -form (unstretched Kynar 300⁽¹⁰⁾) exhibited such a large initial response which then decays upon annealing. When poled in the more conventional way by applying a potential across a film to evaporated electrodes on both sides, essentially no response is observed. The copolymer (Kynar 7200⁽¹⁰⁾) exhibits about the same response as is obtained in conventional poling (see Fig.4) and the decay at 100°C is similar to samples poled conventionally at room temperature. We do not yet understand the decay process. The homopolymer, PVDF, which contains both α and β crystal forms as a result of biaxial stretching (capacitor grade K-F⁽¹⁰⁾) loses about one-half its activity within 5 minutes at 100°C and still retains 43% after 11 days at this temperature. These results suggest to us the possibility that the non-polar crystal form can be made pyroelectric in this way but that it is less stable than the polar form. We did not observe any changes in the IR spectrum of the unoriented Kynar 300⁽¹⁰⁾ as a result of the poling but this is not necessarily in

conflict with Southgate's results since the most pronounced changes are observed at much higher fields than we employed. An x-ray scan does show a shoulder at about $20.8^\circ 2\theta$ (Cu K_α) which is not there in the unpoled data and which may be the 110 and 200 reflection of a β phase. The shoulder remains after annealing for one hour at 100°C . These results are preliminary and must be repeated and extended, before conclusions can be reached. However, they imply that understanding of polymer piezoelectricity in PVDF can be greatly advanced by this line of research.

Table I. Saturation polarization of copolymer films compared with maximum to be expected.

<u>Fractional Crystallinity</u>	<u>Measured Saturation Polarization (Fig.6), $\mu\text{C}/\text{cm}^2$</u>	<u>Calculated Maximum Polarization (Eq.2), $\mu\text{C}/\text{cm}^2$</u>		
		<u>$\gamma = 1$</u>	<u>$\gamma = 2/3$</u>	<u>$\gamma = 1/3$</u>
0.35	1.4	4.2	2.8	1.4
0.43	1.8	5.1	3.4	1.7

Table II. Pyroelectric coefficient resulting from corona poling at room temperature.

<u>Sample</u> (a)	<u>Crystal form</u>	pyroelectric coefficient, nC/cm ² K	
		<u>before annealing</u>	<u>annealed 1 hr. at 100°C</u>
Kureha K-F PVDF	$\alpha + \beta$	2.8	1.4
Pennwalt Kynar 300 PVDF	α	1.6	0.08
Pennwalt Kynar 7200 PVDF-TFE	β	2.3	0.1

(a) See reference 10

Figure Captions

- Figure 1. Pyroelectric coefficient vs. electric field applied to form the electret. The measurements were made at room temperature under short-circuit conditions. ● PVC poled at 80°C; ■ PVDF-TFE copolymer poled at 60°C.
- Figure 2. Recorder trace showing pyroelectric current and temperature as a function of time from which the pyroelectric coefficient is determined.
- Figure 3. Recorder trace showing piezoelectric current and pressure as a function of time from which the piezoelectric coefficient is determined.
- Figure 4. Pyroelectric coefficient of melt-quenched films of Kynar 7200 as a function of applied field during poling. ■ 0°C, Δ 23°C, ○ 60°C.
- Figure 5. Piezoelectric coefficient vs. electric field for copolymer films of different degrees of crystallinity, χ . Results are for duplicate films poled at room temperature. ○, ● $\chi = 0.43$; ■, ■ $\chi = 0.35$.
- Figure 6. Polarization required to account for piezoelectric coefficients of Fig. 5 according to Eq.(1). Data points are averages of the duplicate samples in Fig. 5. ○ $\chi = 0.43$; ■ $\chi = 0.35$.
- Figure 7. Schematic representation of folded-chain crystallites of PVDF in the polar crystal form surrounded by non-crystalline regions. Rotation about the chain axis within the crystals on the left would allow reorientation in an applied field and result in the polarization on the right.

Figure 8 Schematic representation of polymer crystallites oriented with polymer chain axis normal to the plane of the paper on which it is shown. (a). Unpoled polymer film, (b) poled polymer with no limitation on angle of rotation about chain axis. The rectangles represent a projection of the unit cell onto the ab plane drawn about a central position to indicate the translational motion which must follow in order to maintain the crystal structure, (c) poled polymer allowing only 180° rotation.

Figure 9. Raman spectra from two different regions of the same copolymer film. No poling voltage has been applied in either case.

Figure 10. A sketch of the film-electrode-epoxy composite used for optical microscopy.

Figure 11. Charge transfer between electroded surfaces of copolymer film 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. [FWHM is abbreviation for full width at half-maximum.]

Figure 12. Charge transfer between electroded surfaces of copolymer film as a function of time following a heat impulse on one surface of the film; (a), (b), and (c) as in Fig.11. Poling conditions were 255 kV/cm at 101°C for five minutes. Copolymer film is 47 μm thick.

Figure 13. Spatial distribution of polarization in copolymer films from Figs. 11 and 12. The polarization is largest at the electrode that was positive during poling.

Figure 14. 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) poly(vinylidene fluoride) homopolymer poled for 30 minutes at 110° and 800 kV/cm. Pens for charge and temperature are physically offset.

Figure 15. 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 16. The apparent pyroelectric coefficient at various points in time from the curves in Fig. 15. 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 by integration of either curve in Fig. 15. Time axis refers to point of departure of current from zero in Fig. 15.

Figure 17 Decay of pyroelectric coefficient of PVDF-TFE copolymer as a function of time stored at 60°C . \circ quenched film, poled at 0°C , 500 kV/cm; \bullet quenched film poled at 60° , 300 kV/cm; \bullet slowly cooled film, poled at 60° , 500 kV/cm; Δ slowly cooled film, poled at 80°C , 500 kV/cm.

Figure 18 Pyroelectric coefficient of PVDF-TFE copolymer poled during crystallization as a function of time stored at various temperatures. Δ aged at 60°C ; \circ aged at 80°C ; \bullet aged at 100°C . \bullet data of same symbol taken from Fig. 17 for comparison. (Three points corresponding to aging times of less than 30 minutes at 60°C are off the scale of this plot).

Figure 19. Copolymer film between crossed polaroids. The lighter portion was crystallized in an electric field.

Figure 20. X-ray diffractometer scans of copolymer film. Solid line refers to data obtained from the portion of the sample which crystallized in an electric field, broken line refers to data obtained from the unpoled region of the same film. The reflection in the regions from 30° to $48^\circ 2\theta$ are very weak and are recorded at a sensitivity 10X larger than the peak near 20° .

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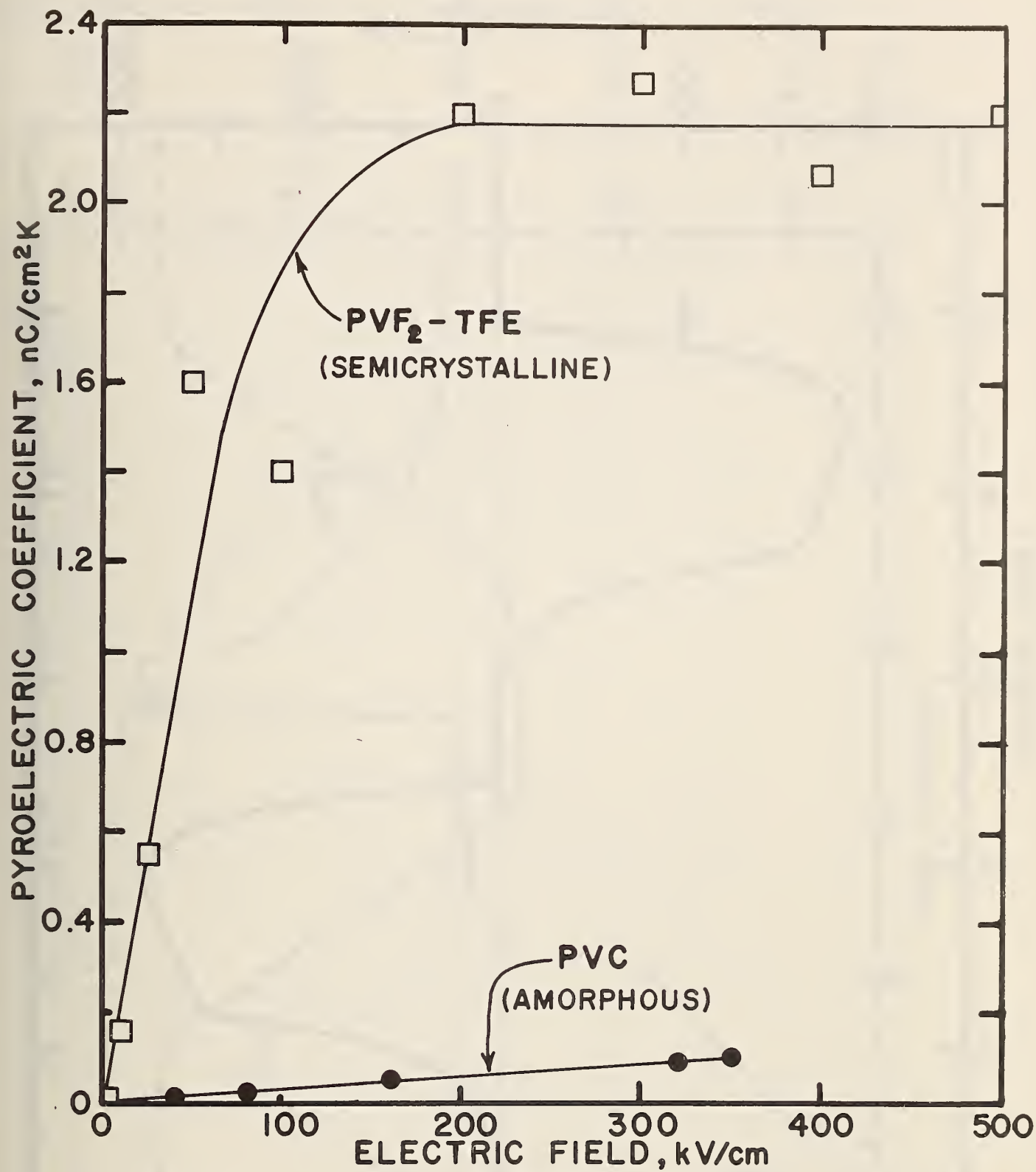


FIG. 1

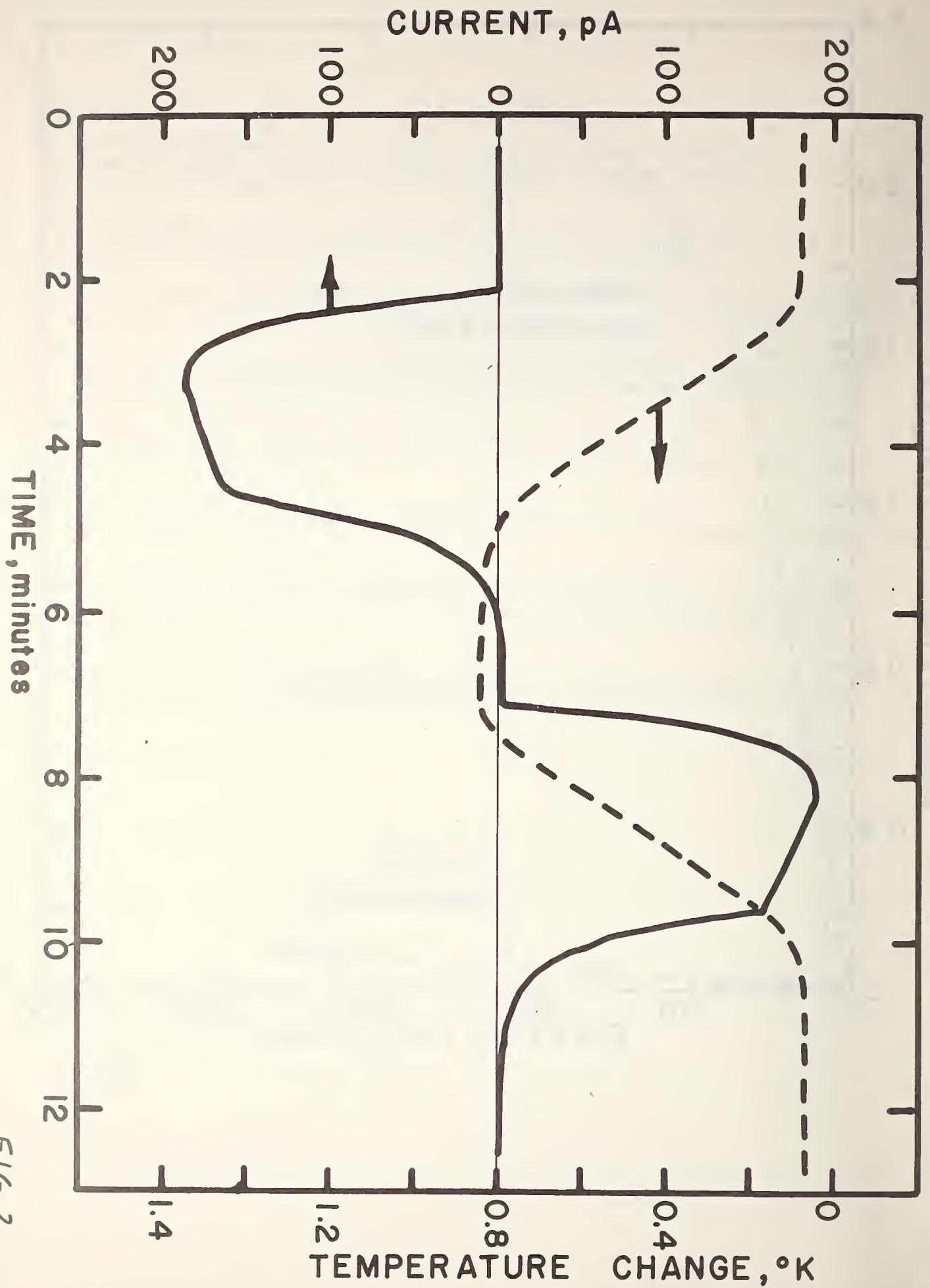


FIG. 2

PRESSURE

psi $\frac{\text{Nm}^{-2}}{10^5}$

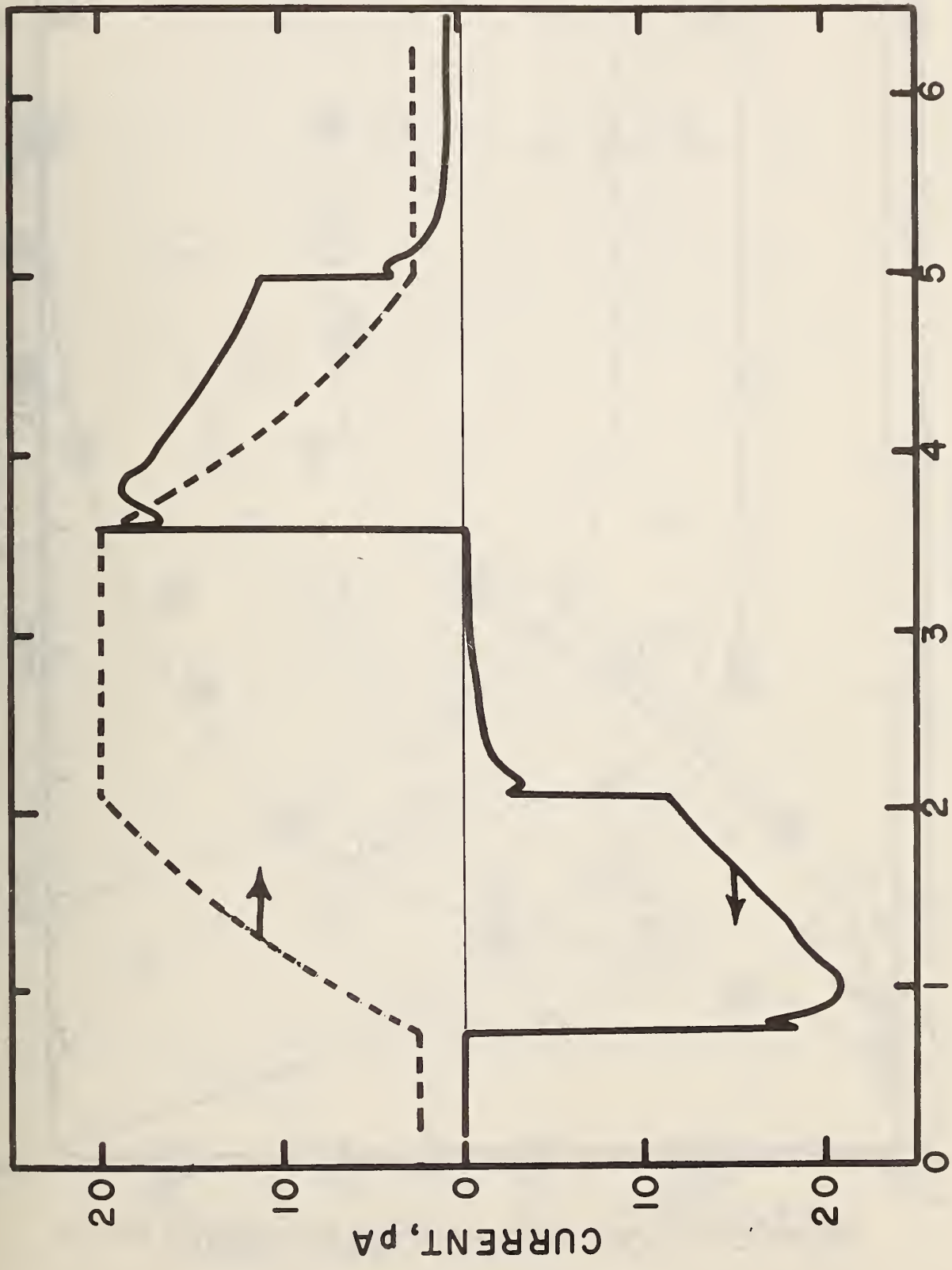
180 12.4×10^5

140 9.65×10^5

100 6.89×10^5

60 4.13×10^5

20 1.38×10^5



TIME, minutes

FIG. 3

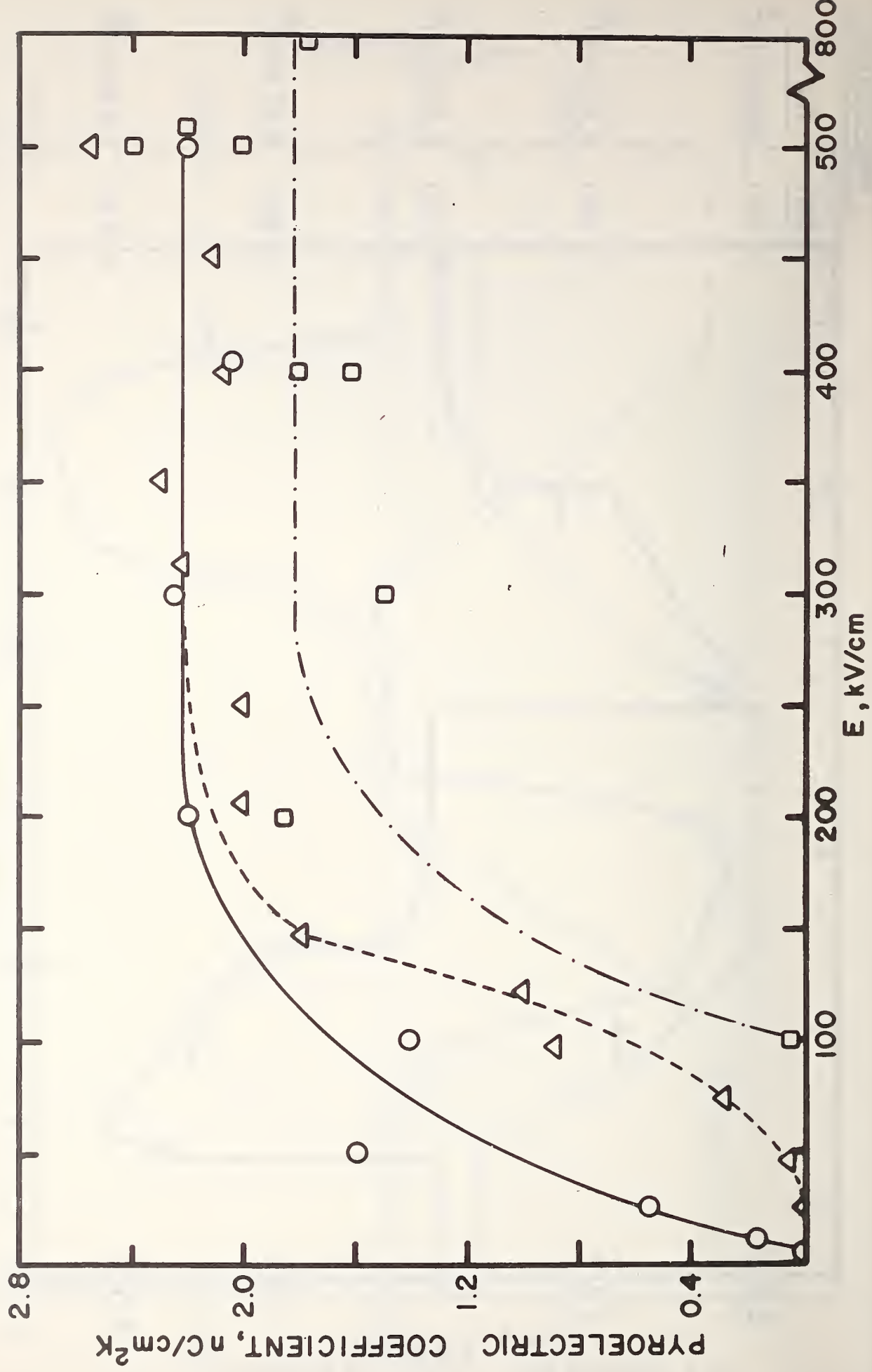


FIG. 4

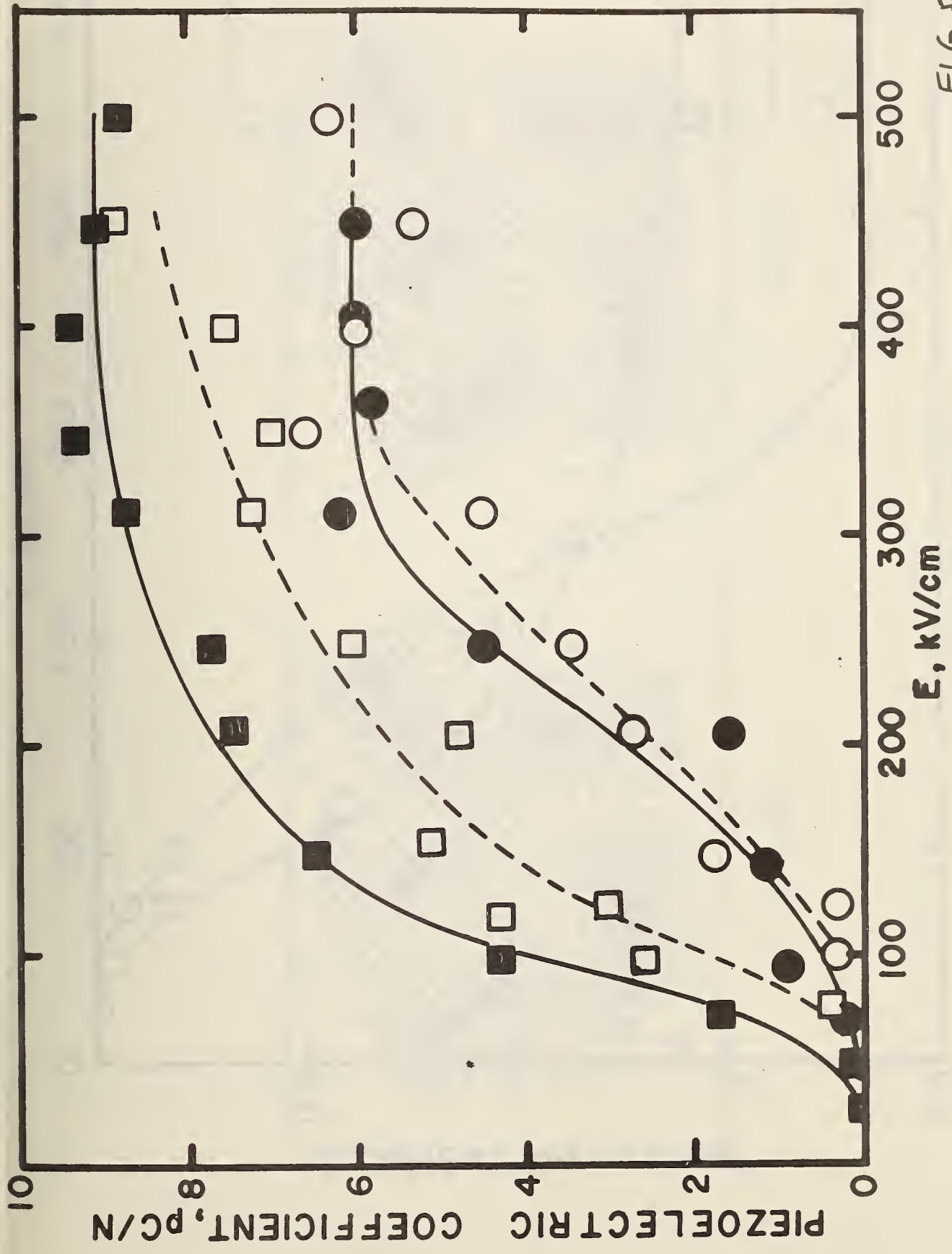


FIG. 5

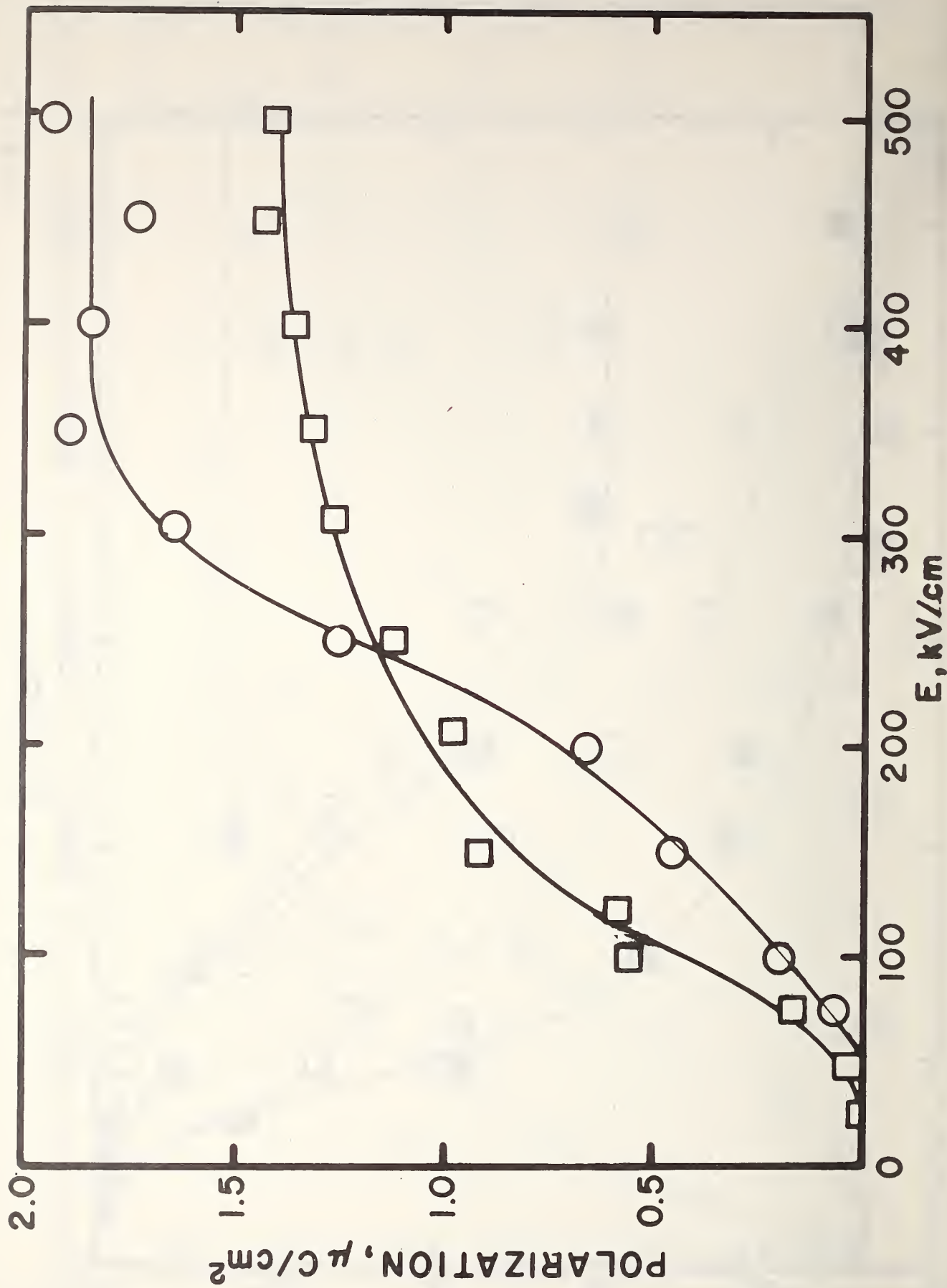


FIG. 6

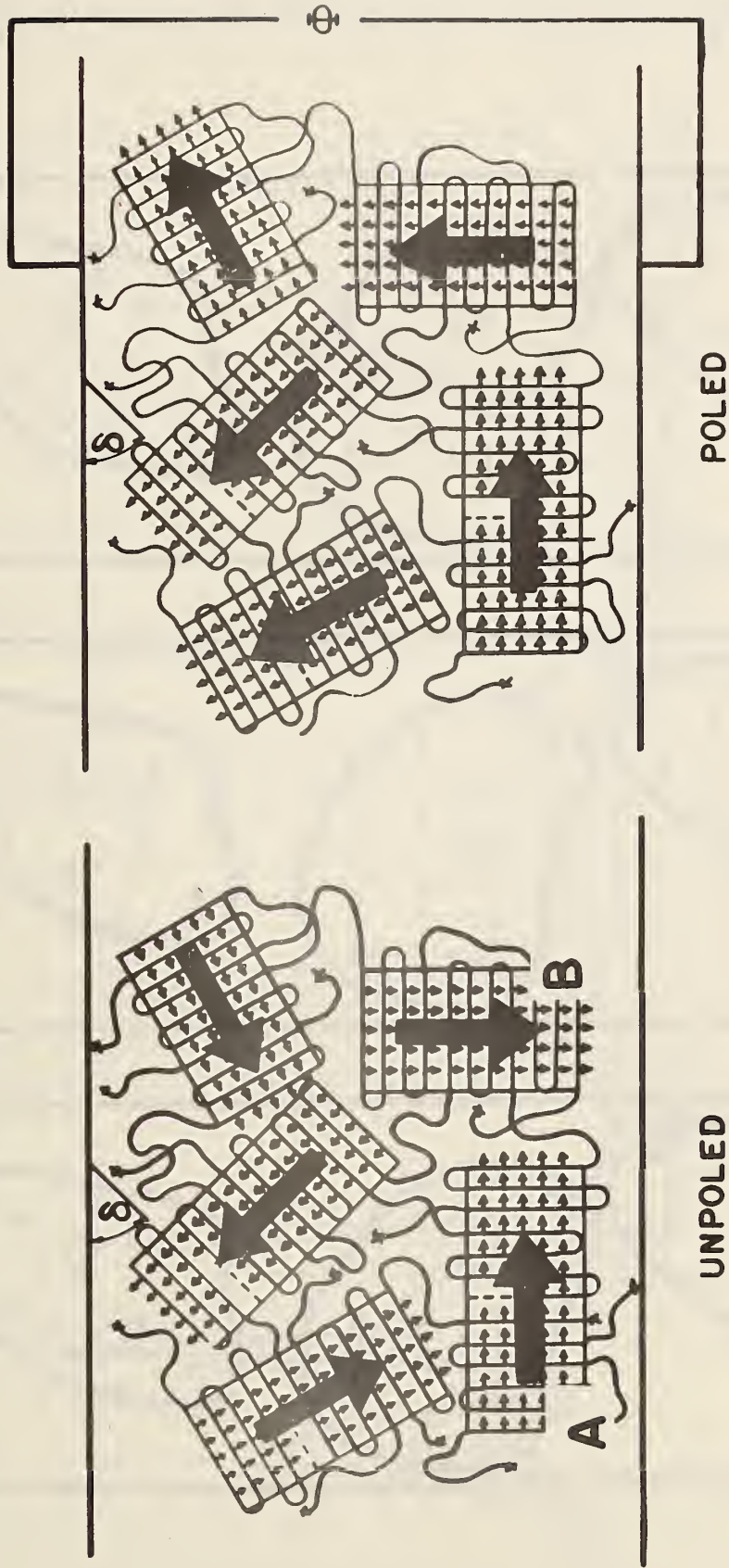


FIG. 7

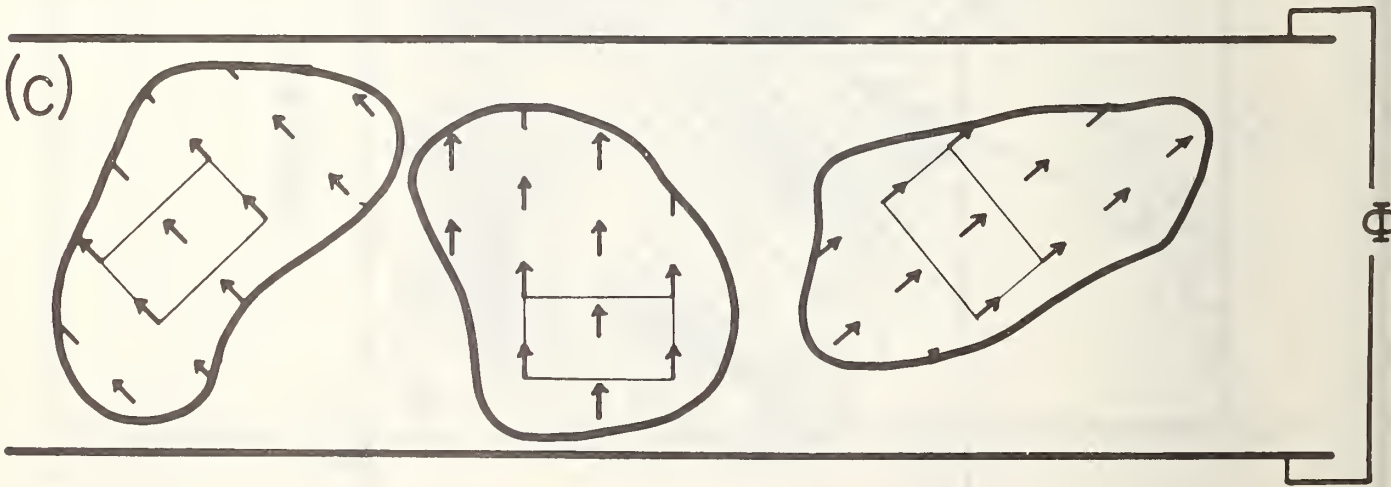
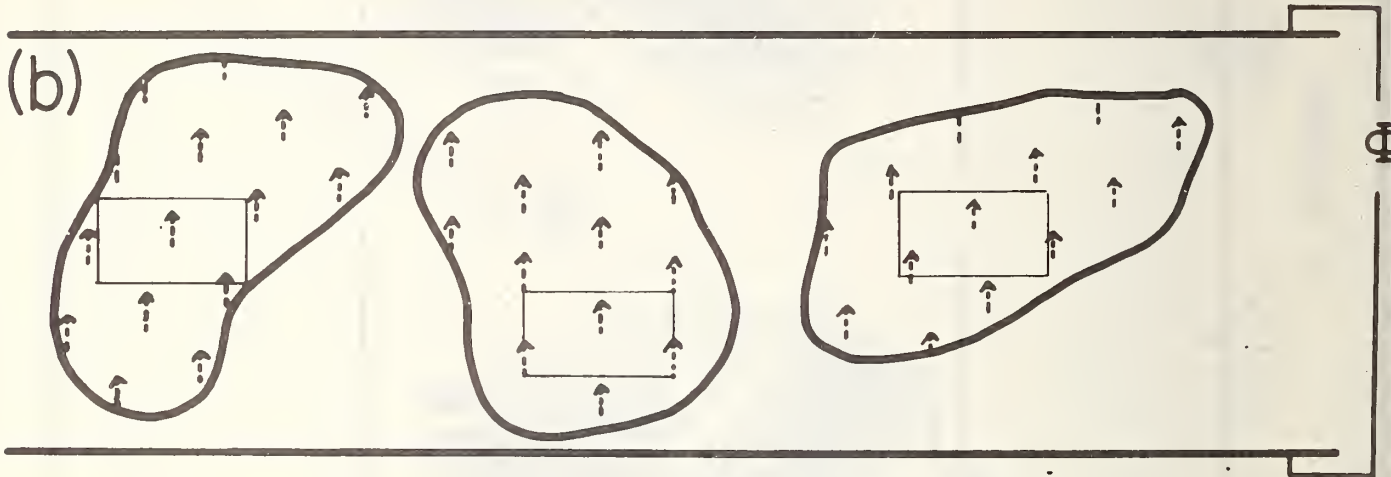
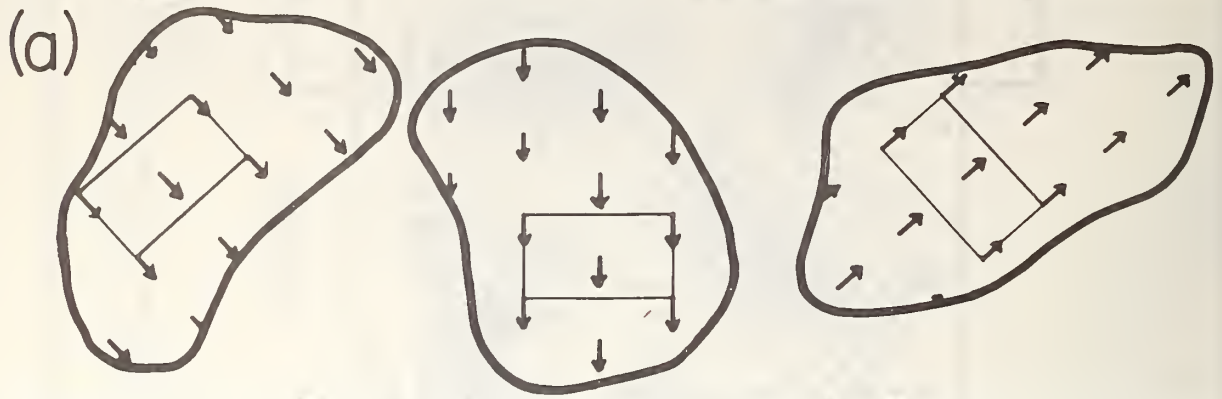


FIG. 8

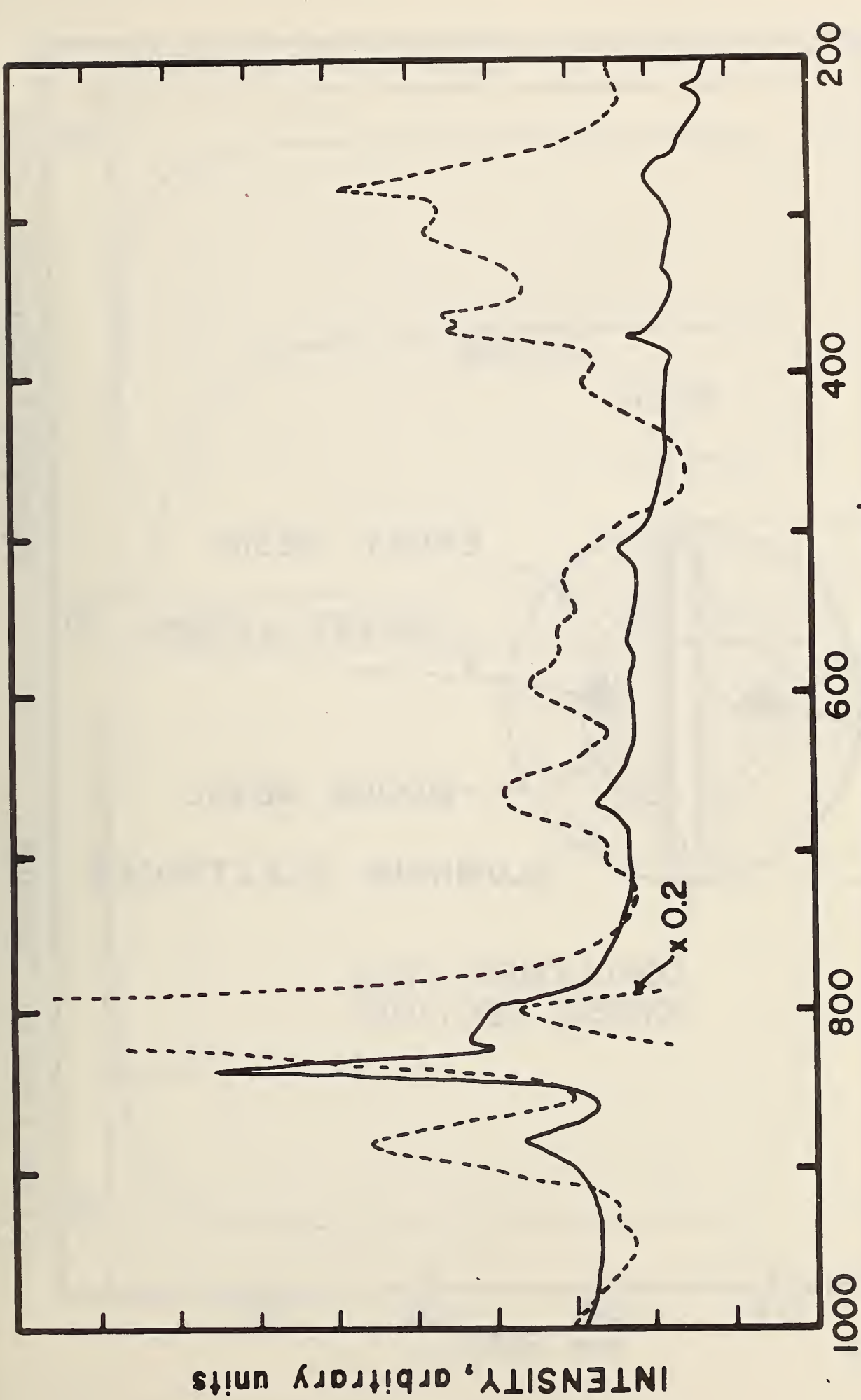


FIG. 9

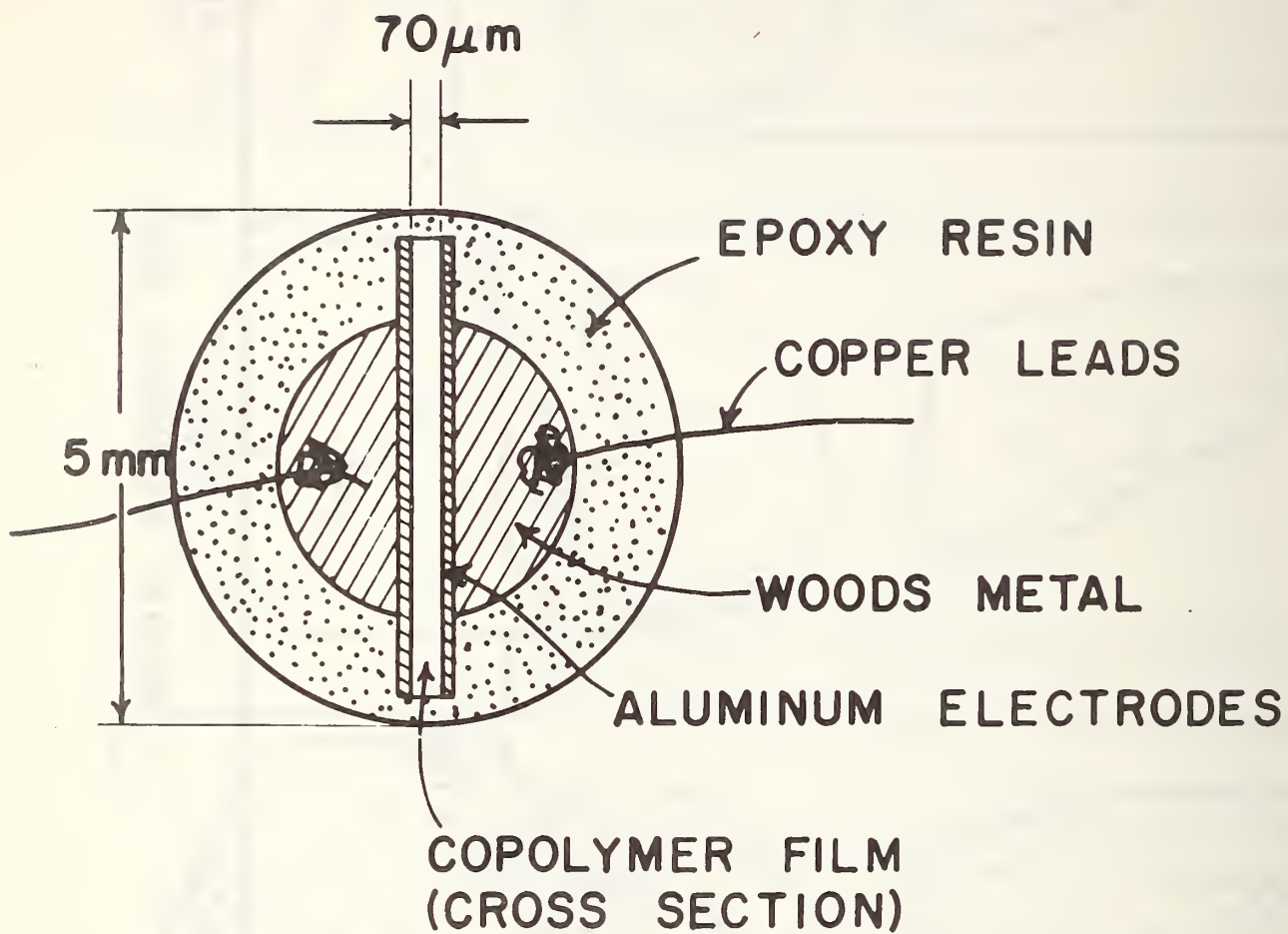


FIG 10

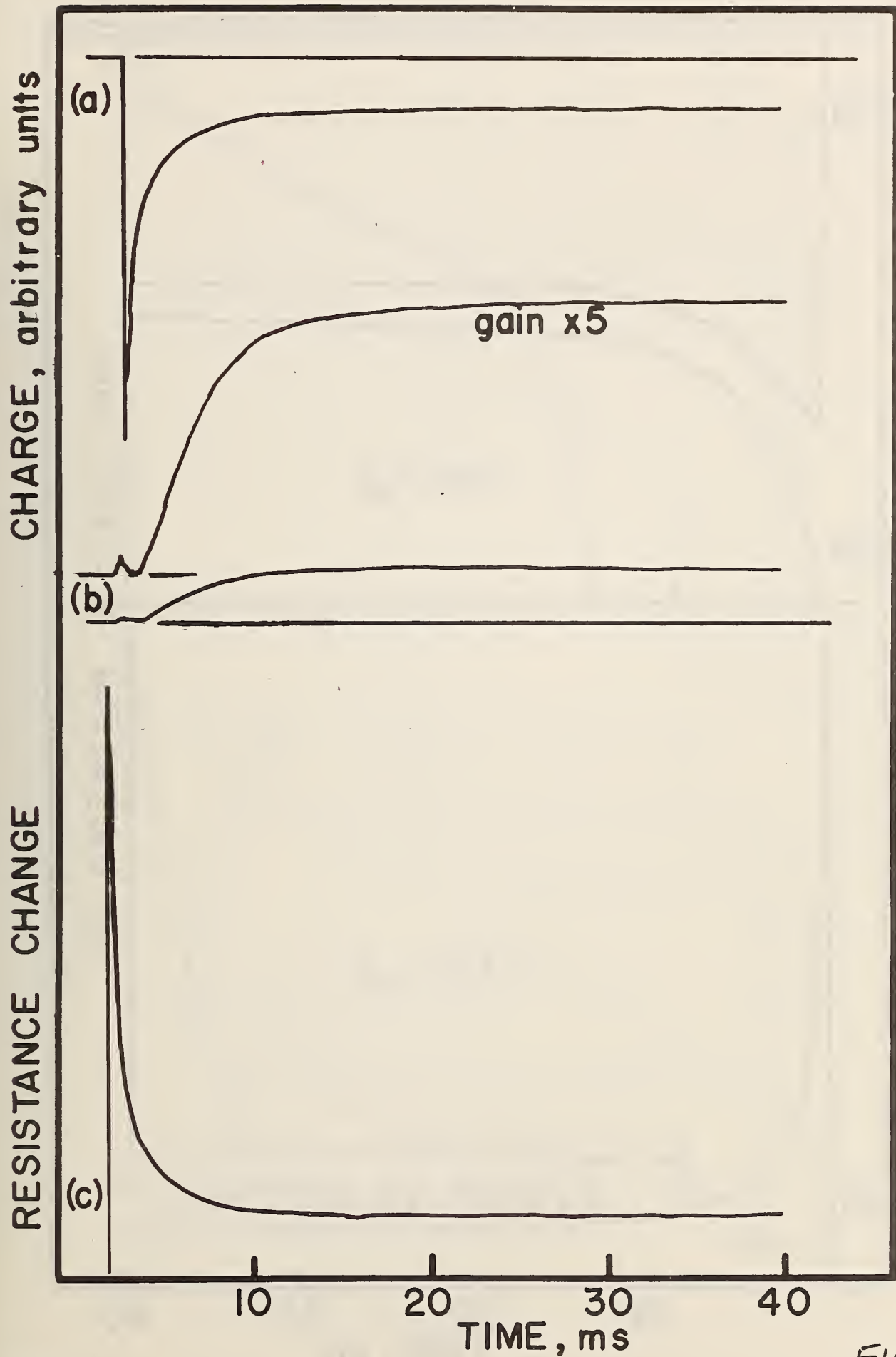


FIG. 11

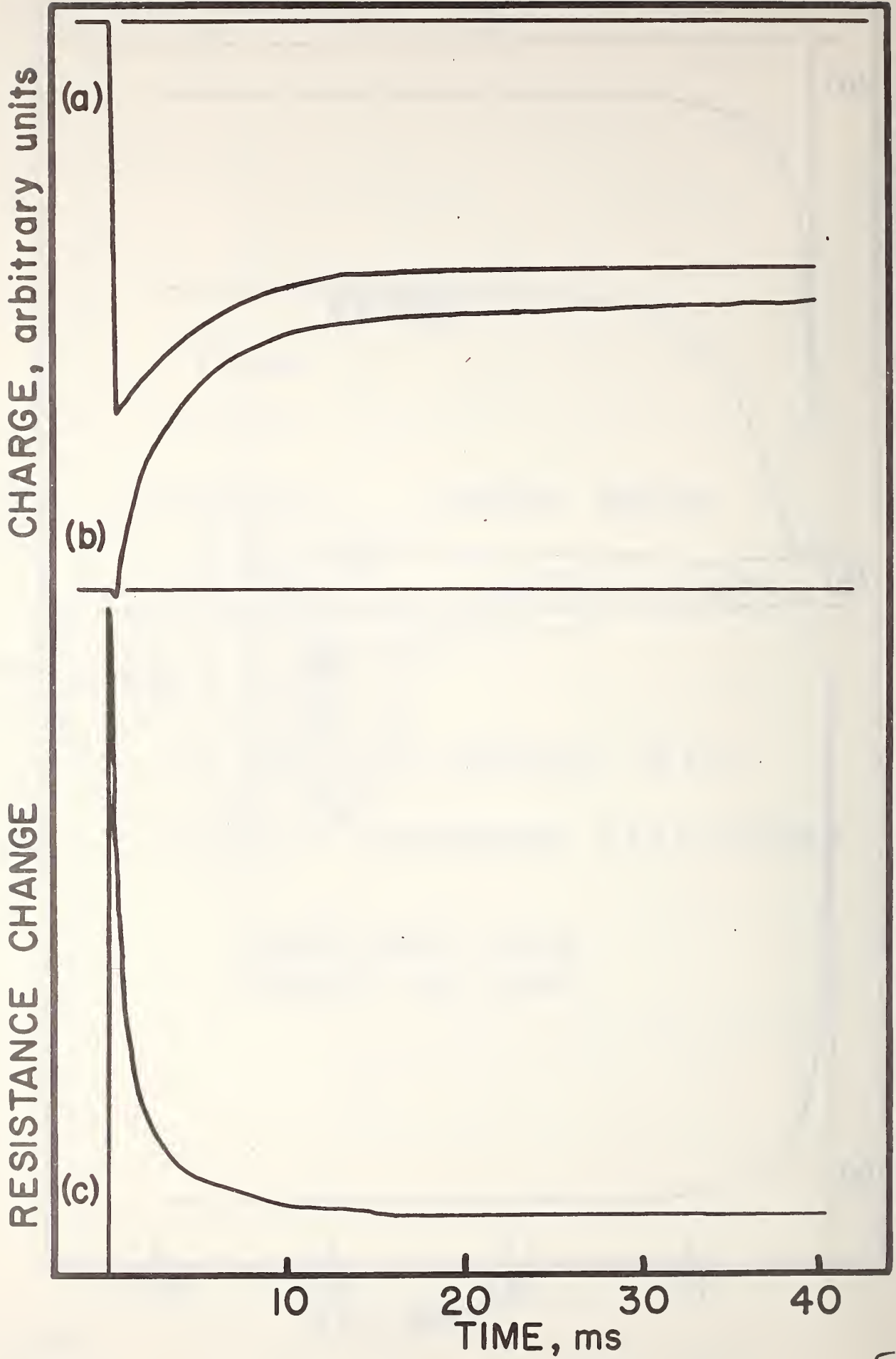


FIG. 12

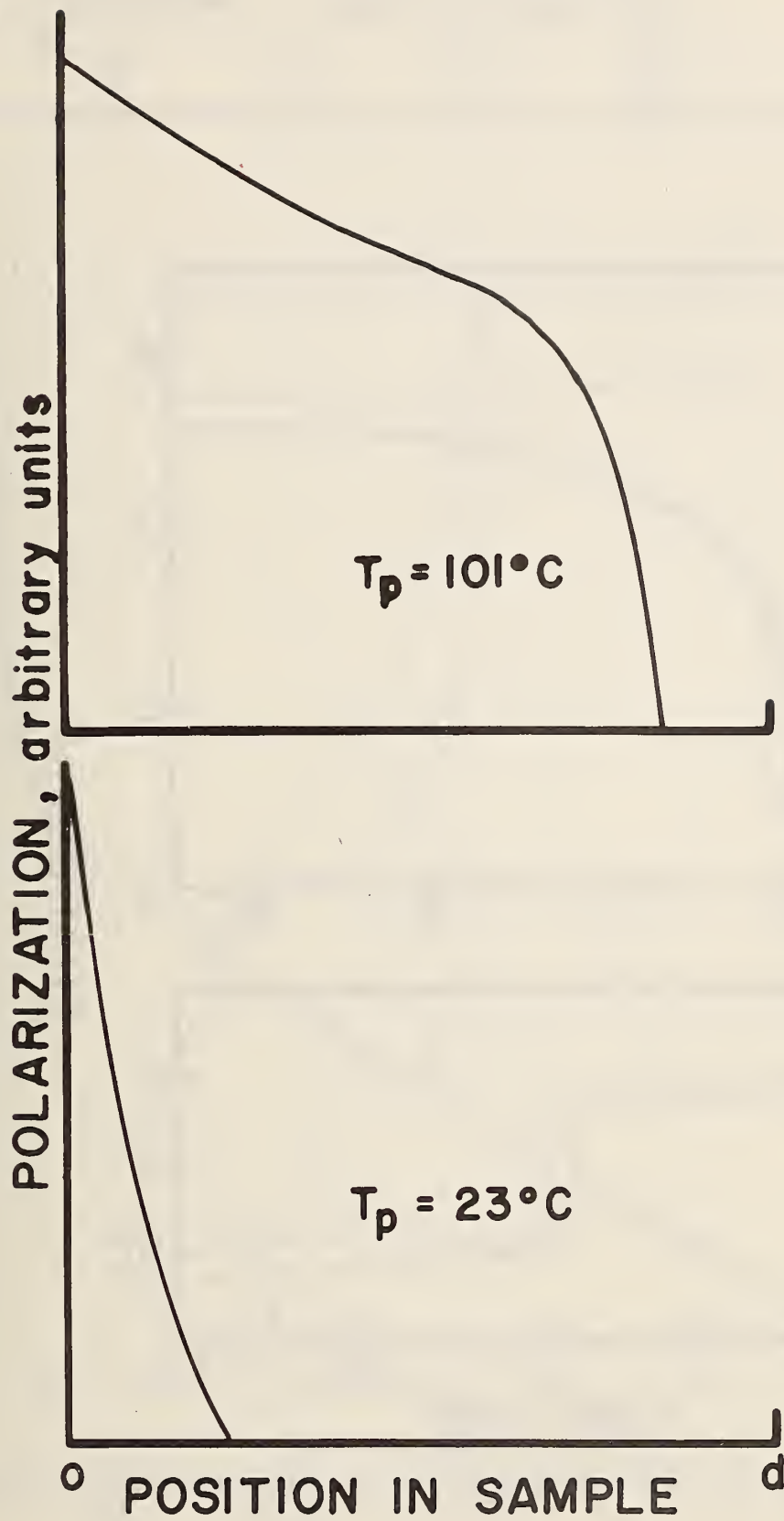


FIG. 13

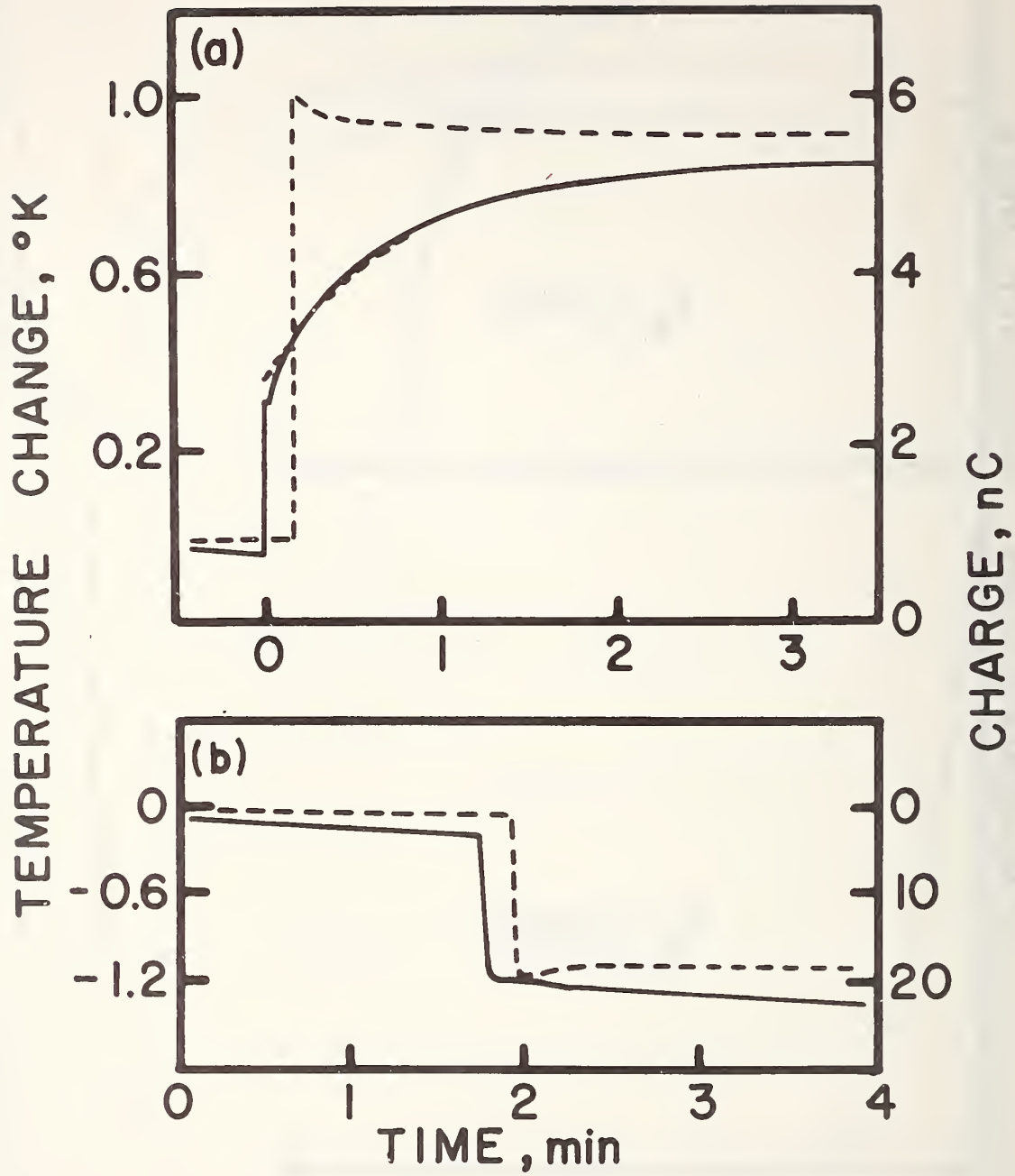


FIG. 14

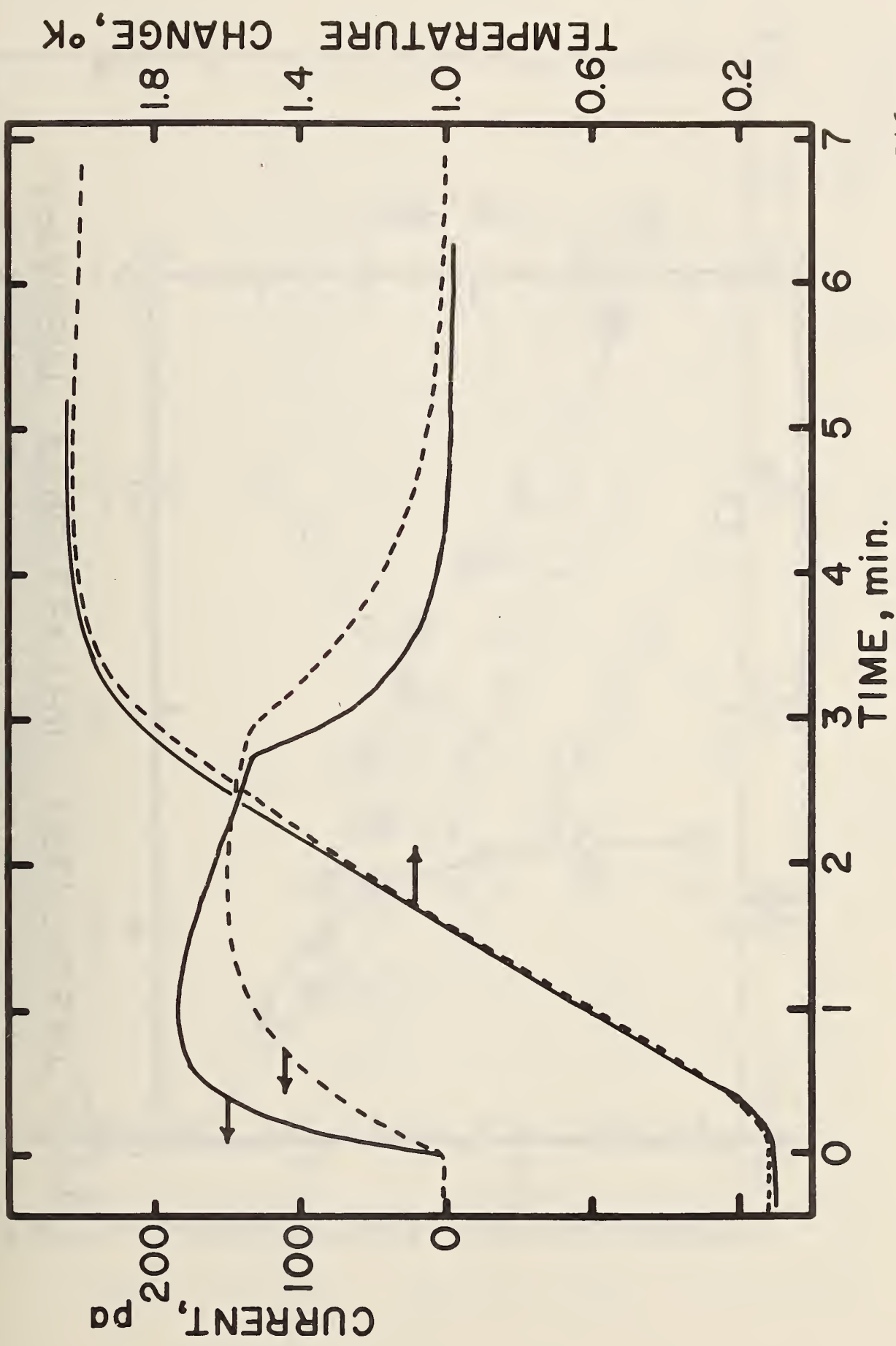
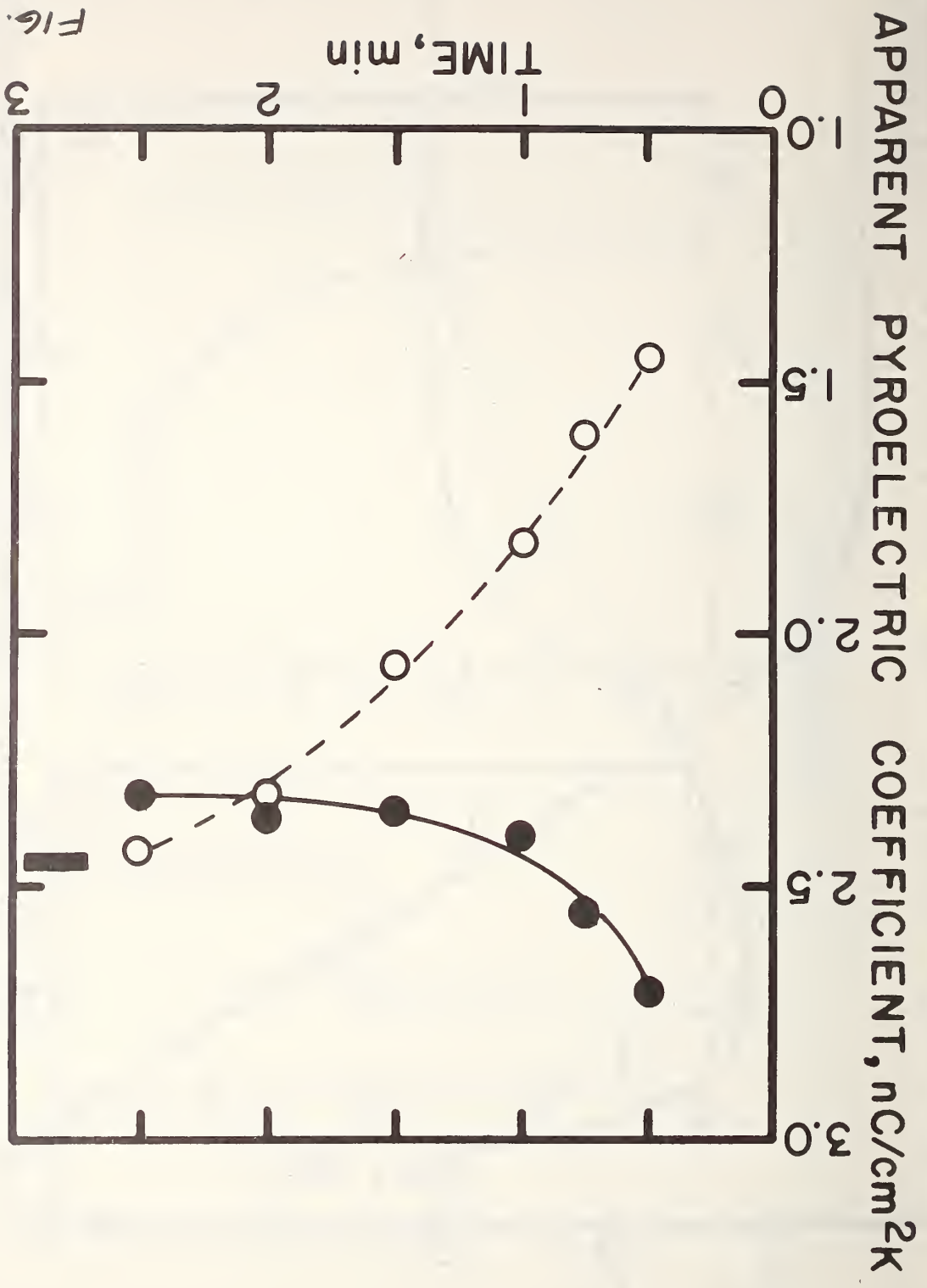


FIG. 15

FIG. 16



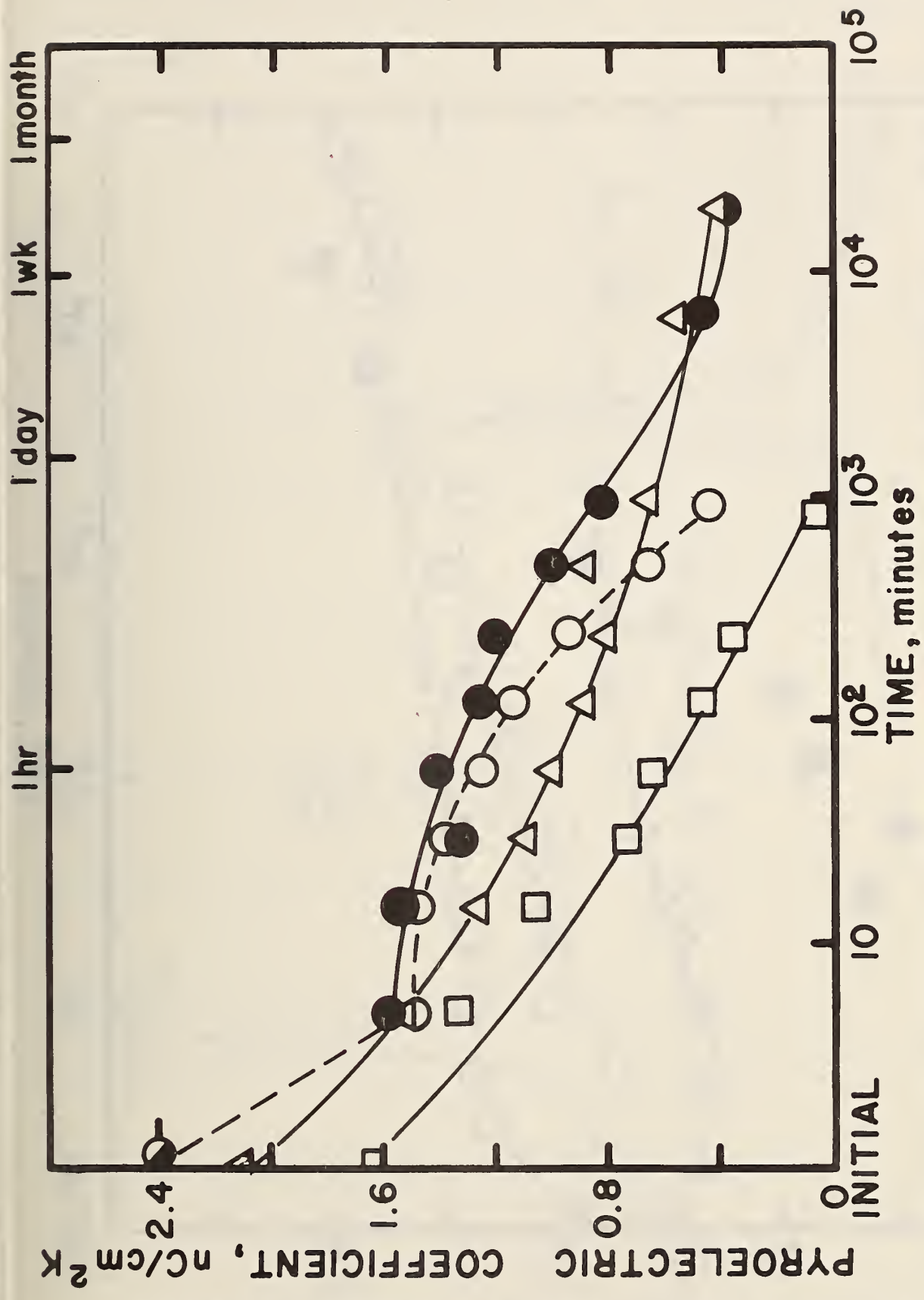
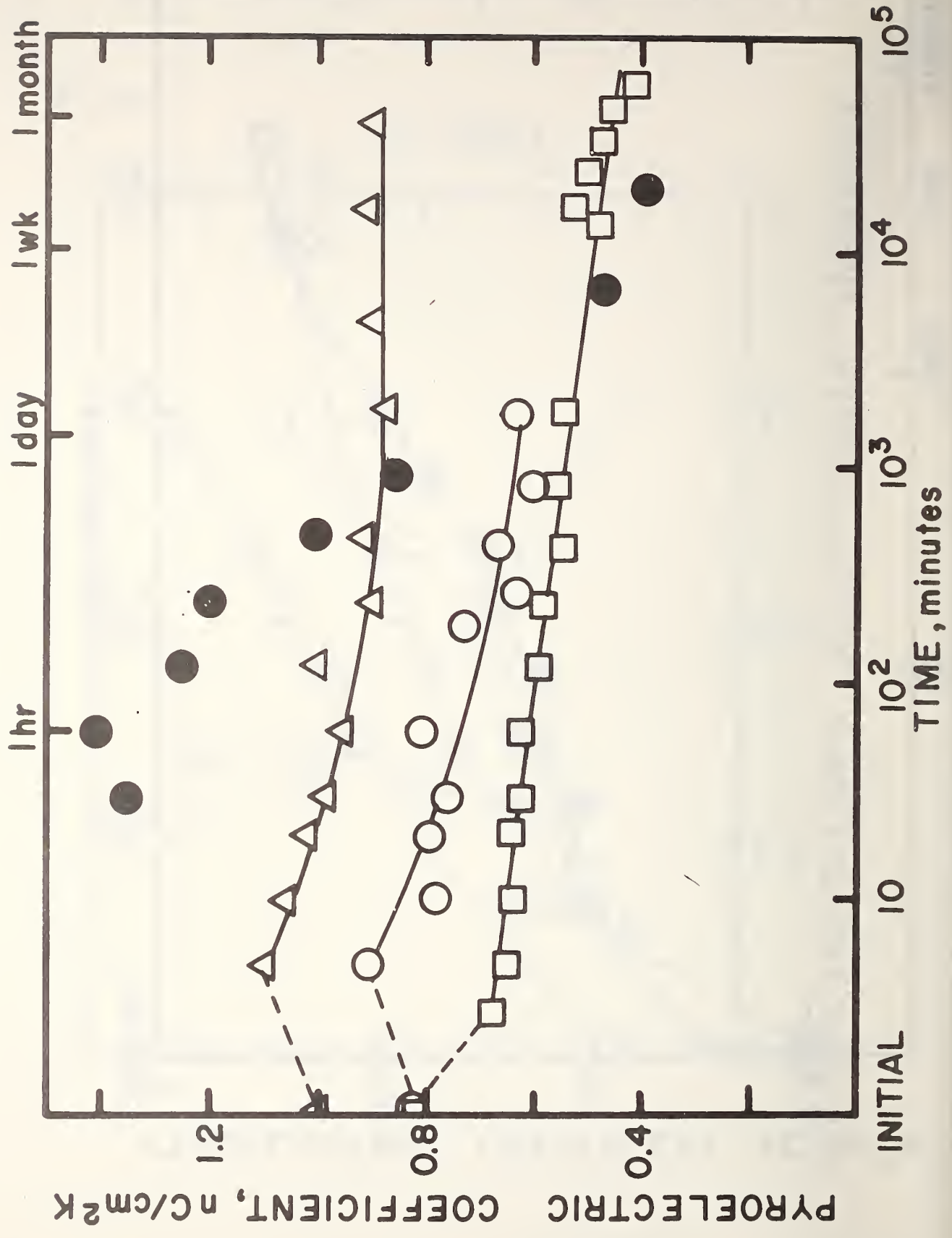


FIG. 17



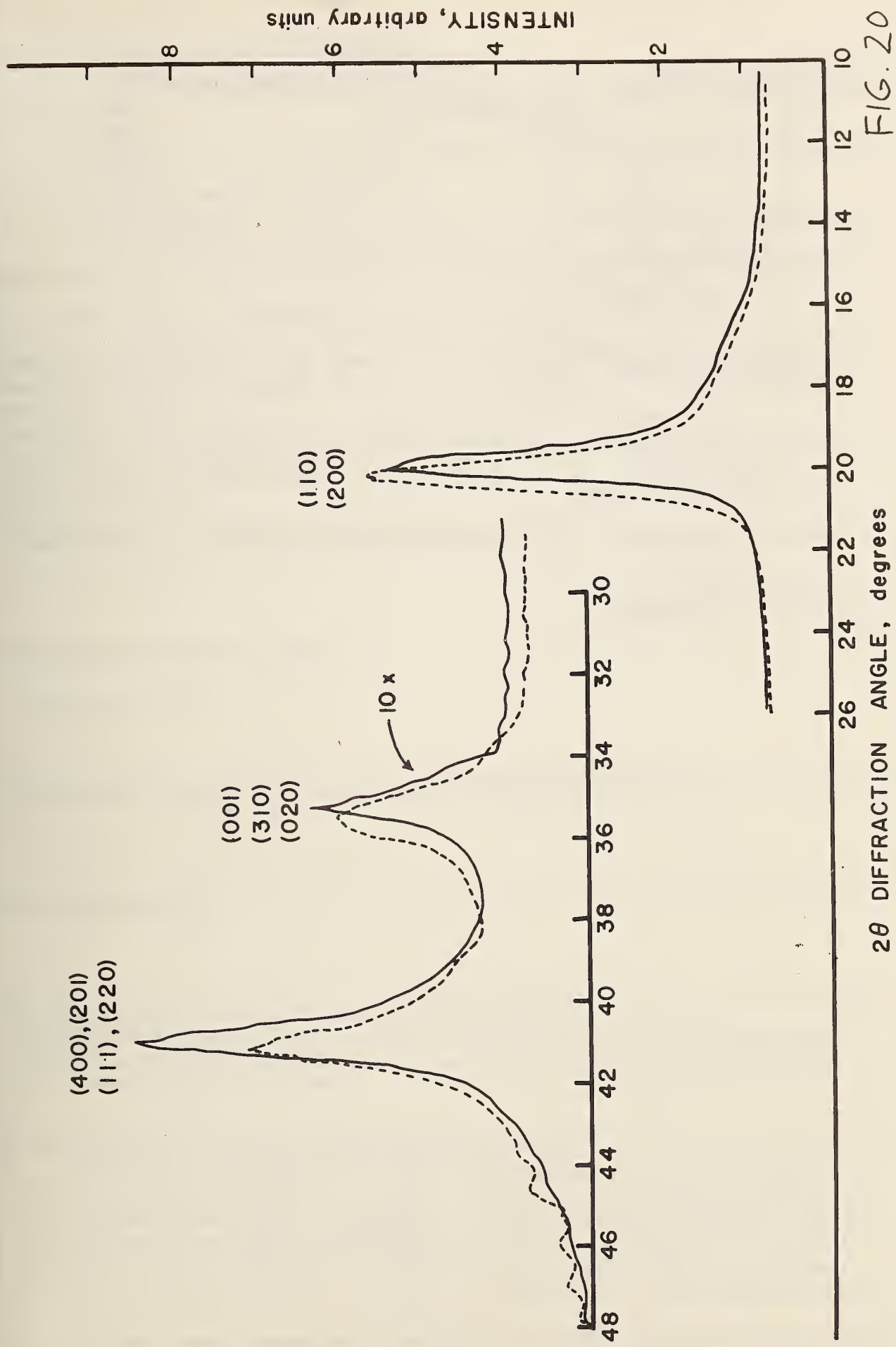


FIG. 20



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between 0° and 80°C. Piezoelectric responses from samples of varying crystallinity are consistent with increased polarization and lower compressibility as the degree of crystallinity is increased.

Thermal pulse experiments reveal that when poled at room temperature, only a thin region near the positive electrode is poled but the thickness of this region increases with an increase in poling temperature.

Copolymer films crystallized from the melt in the presence of a field show greatly improved stability of piezoelectric activity when stored at elevated temperatures compared with samples poled only after crystallization.

The room temperature poling of polyvinylidene fluoride using a corona discharge has been confirmed. Preliminary results are presented which imply that even the non-polar α phase of the polymer may be poled in this way but it is unstable--especially at elevated temperatures.

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