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PIEZOELECTRIC ACTIVITY AND FIELD-INDUCED CRYSTAL STRUCTURE TRAN--ETC(U)

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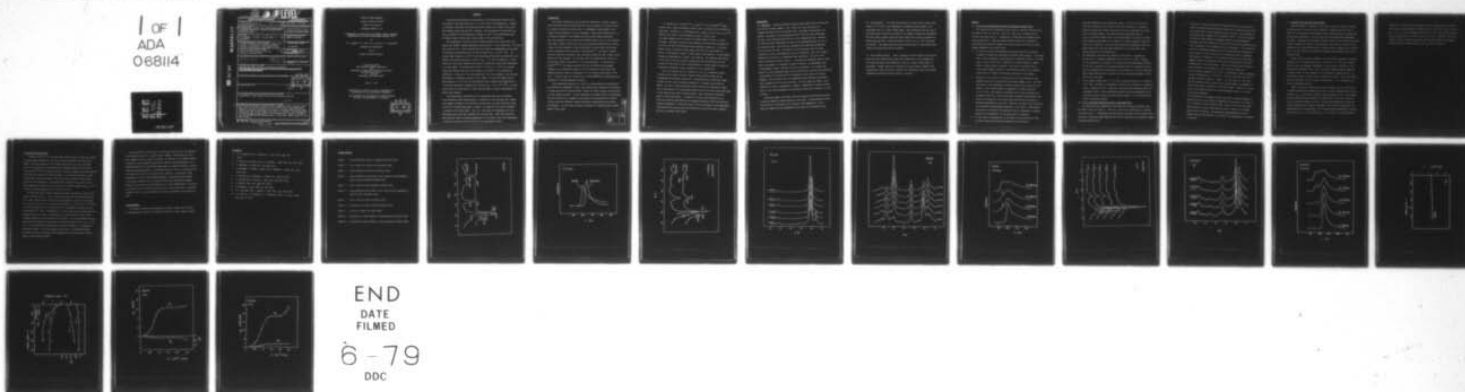
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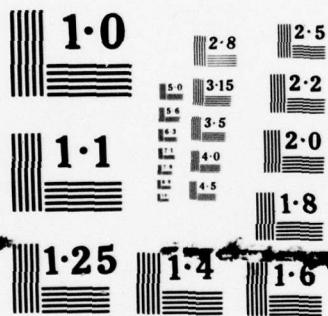
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TECHNICAL REPORT NO. 15

PIEZOELECTRIC ACTIVITY AND FIELD-INDUCED CRYSTAL STRUCTURE
TRANSITIONS IN POLED POLY(VINYLIDENE FLUORIDE) FILMS

by

B. A. Newman, C. H. Yoon, K. D. Pae and J. I. Scheinbeim

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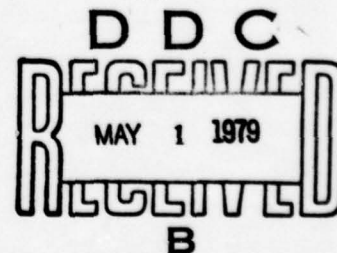
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ABSTRACT

Unoriented and biaxially oriented phase II poly(vinylidene fluoride) films were poled at very high fields up to 4.0×10^6 V/cm at room temperature. Changes in molecular orientation and crystal structure induced by the high-field poling were studied using x-ray and D.S.C. methods. The piezoelectric coefficients d_{31} and e_{31} together with the dielectric response (ϵ' and ϵ'') were determined using a Piezotron Model U (Toyo Seiki, Tokyo, Japan) for the poled films.

The piezoelectric activity did not increase steadily with poling field, but showed four distinct regions depending on poling field. At low fields ($E_p < 10^6$ V/cm), when x-ray and D.S.C. data indicated that the films were predominantly in the phase II structure, the piezoelectric activity was small ($e_{31} < 2 \times 10^{-3}$ c/m²). For poling fields between $1-2 \times 10^6$ V/cm the piezoelectric activity was observed to rise rapidly with poling field until a value of $e_{31} \sim 14.5$ c/m² was observed. In this region the x-ray scans indicated that phase II crystallites were being transformed to a polar phase. At poling fields from 2×10^6 V/cm to 4×10^6 V/cm a plateau region was observed with very little change in the value of the piezoelectric coefficient. X-ray and D.S.C. data showed that very little change in the structure and molecular orientation occurred in this region. At the very highest poling field applied (4×10^6 V/cm) the piezoelectric data indicated the commencement of a very rapid increase in piezoelectric activity ($e_{31} \sim 19.5 \times 10^{-3}$ c/m²). At this poling field the x-ray and D.S.C. data indicated that a crystal transformation to phase I had occurred.

The piezoelectric coefficients of the unoriented films was not measured. X-ray diffraction data indicated that, in addition to the structural and orientation changes occurring in the biaxially oriented film, an x-ray reflection, which could not be indexed using phase I, phase II or phase III unit cells, increased in intensity with poling field. The D.S.C. data showed the appearance of a new endothermic peak which also increased with poling field. These data indicated that molecular chains oriented perpendicular to the plane of the films transformed to some new structure under the action of the high applied fields.

INTRODUCTION

The unique piezoelectric and pyroelectric properties of poled, oriented poly(vinylidene fluoride)(PVF₂) films have been the subject of intensive study by a number of workers in recent years. A fundamental understanding of the origin of this phenomenon is still incomplete. Many authors assume that it is an inherent property of the polymer and arises from volume polarization. PVF₂ can crystallize in at least three different forms, and it is the oriented polar phase (phase I) which gives rise to the greatest piezoelectric activity. A model has been proposed in which polarization of poled films results from dipole orientation within the phase I crystallites⁽¹⁾. The phase I crystal structure certainly indicates a very high dipole moment per unit volume as compared with other polymers. On the other hand, the piezoelectric activity of α -phase PVF₂ (which is non-polar) is not inconsiderable. It has been suggested^(2,3,4,5) that charge injection from the electrodes and subsequent trapping in the crystalline regions or at the interface of the crystal and amorphous material might be responsible for the observed polarization of the film. A recent study by H. Sussner and K. Dransfeld⁽⁵⁾ certainly demonstrates the importance of the metal-polymer interface.

These mechanisms, proposed as a basis for understanding the piezoelectric and pyroelectric phenomenon in PVF₂, carry implications regarding the properties of films which are not oriented phase I films; the films usually studied because of their highest activity. In this laboratory a systematic series of experiments have been carried out to examine the piezoelectric and pyroelectric behavior of PVF₂ films with different crystal structures, morphologies, and molecular orientations. In this study we report our results for unoriented and oriented phase II PVF₂ films.

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H. Burckard and C. Pfister⁽⁶⁾, H. Sussner⁽⁷⁾ and H. Ohigashi⁽⁸⁾ demonstrated that a large piezoelectric effect could be obtained even from Phase II PVF₂ films. Recently, D. K. Das-Gupta and K. Doughty and also Davis et al.⁽¹⁰⁾ reported that using a corona charging technique, crystal structure phase changes could be induced in oriented phase II films. At lower voltages, a new phase, with unit cell dimensions identical with the phase II unit cell but with a different molecular packing was reported. It was suggested that by a rotation of PVF₂ chains about the chain axes under the action of high electric fields a "polar" phase II was produced. At the highest voltages a transformation to phase I was observed. The important implication of this work is that the observed unexpectedly high piezoelectric activity of phase II films results from a transformation to "polar" phase II caused by poling, with concomitant dipole orientation in the crystallites.

One of the reasons for this study was to test the correlation between orientation and crystal structure changes resulting from poling and the accompanying piezoelectric properties. Although previous studies have demonstrated that the corona discharge technique is a convenient and effective method, in order to obtain more quantitative results with implications applying to films poled in the conventional manner we poled our films using electrodes so that poling fields were accurately known. Both oriented and unoriented phase II films were studied. In addition to using x-ray diffraction, the films were studied using differential scanning calorimetry (DSC) and dielectric constant measurements. Films were poled at various voltages at room temperature, characterized after poling, and the piezoelectric stress and strain constants d_{31} and e_{31} measured after poling.

EXPERIMENTAL

(a) Materials: Biaxially-oriented capacitor-grade Kureha PVF₂ 25 μ films were used for the oriented samples. Fig. 1 shows the x-ray reflection and transmission scans for the as-received film. Both phase II and phase I are present. The phase II shows orientation since (110) and (020) reflections are seen in the reflection mode but not in the transmission mode. Moreover the (002) and (021) reflections are seen in the transmission mode but not in the reflection mode. This would be consistent with chain axis orientation in the plane of the film. The phase II is also oriented since the (001) reflection is seen in transmission but not in reflection. The (110), phase I reflection is seen both in transmission and reflection. The D.S.C. scan taken at 10°C/min is shown in Fig. 2 and shows an endothermic peak at 178°C, which would appear to correspond to phase II melting. An endothermic peak corresponding to phase I melting could not be discerned. We conclude that phase II is the predominant phase in the oriented film, and that the intensities corresponding to the reflection and transmission scans cannot be directly compared. The intensities for the transmission mode represent much greater values compared with the reflection mode. For this reason the phase I (110) reflection is seen in transmission. However a comparison of intensity ratios (001) to (110) from transmission and reflection shows that the phase I is also oriented.

Unoriented phase II 25 μ PVF₂ films were prepared by melting and crystallizing the biaxially oriented films in a hot press. Crystallization at 130°C was carried out, followed by slow cooling to room temperature. Fig. 3 shows the reflection and transmission x-ray scans for the prepared film.

(b) Poling methods: The films were subjected to high electric fields under vacuum ($\sim 10^{-5}$ Torr) at room temperature by applying large voltages to the electrodes from a D.C. high voltage supply. When evaporated gold was used as electrodes great difficulty in poling at the highest voltages was encountered. For this reason a highly conducting silver paste which could be stripped off after poling was used. Films were poled at fields up to 4×10^6 V/cm using this method. The poling times were long (several hours) so that effects associated with poling time were not expected.

(c) Film characterization: After stripping the silver paste from the poled films they were characterized using x-ray diffraction in both transmission and reflection modes (CuK α radiation), and D.S.C. using a Perkin Elmer I B instrument. Dynamic dielectric constants and elastic moduli, together with piezoelectric stress and strain constants were determined using an instrument commercially available from Toyo Seiki, a Piezotron.

RESULTS

(a) D.S.C. and X-Ray Diffraction Data for Biaxially Oriented Films

The reflection and transmission x-ray scans for the poled oriented films are shown in Fig. 4(a) and (b). The D.S.C. scans with a heating rate of $10^{\circ}\text{C}/\text{min}$ are shown in Fig. 5. Essentially the same data was obtained using other heating rates. These data taken together reveal that a variety of orientation and structural changes occur during poling, the extent of these changes depending on the poling field.

1. In the D.S.C. scans the endothermic peak associated with the melting of phase II crystallites decreases and broadens after poling. At the same time a second endothermic peak appears with a maximum at 185°C . For films poled at lower fields this is observed as a small shoulder, at higher fields a distinct peak is observed. This data is consistent with a field induced damage to phase II crystallites, leading, at the highest poling field, to changes in the crystal structure of the polymer.
2. Inspection of the phase II reflections in the x-ray diffraction scans indicates that both orientation and structural changes occur. The (020) reflection in the transmission increases steadily with the poling field whereas in the reflection mode it disappears at fields as small as $1.6 \times 10^5 \text{ V/cm}$. This would be consistent with a b-axis orientation in the plane of the film. Since the biaxial orientation already places the c-axis in the plane of the film this would entail that the a-axis is oriented perpendicular to the film. Since for the phase II the direction of the dipoles are approximately parallel to the a-axis. These results then would be consistent with hypothesis that an orientation of dipoles parallel (or antiparallel) to the poling field is produced.
3. If the a-axis is perpendicular to the plane of the film then the (100) and (200) reflections should be enhanced in the reflection

scans and decreased in the transmission scans. In fact this is true for the (200) reflection but not true for the (100) reflection. A change in relative intensities of these reflections can only be explained as arising from a structural change. This observation was previously made by Davis et al⁽¹⁰⁾ who proposed that a new crystal phase, with unit cell dimensions identical with phase II, is formed, by a simple rotation of chains to form a polar structure. Our data would confirm this explanation, with the added feature that our data shows orientation of the polar phase, with dipoles parallel to the poling field.

4. The diffraction scans show the presence of some phase I, although not giving rise to a separate endothermic peak in the D.S.C. scans. Changes in the orientation of the phase I can be seen from the diminishing intensity of the (110) reflection with increasing poling field for transmission scans. This is accompanied by an increasing of the intensity of the (001) reflection. These observations would be consistent with an increasing alignment of chain axes in the film plane.
5. At the highest poling field (4×10^6 V/cm) a marked increase in the intensity of the (001) reflection in transmission and the (110) reflection in reflection occurs. Moreover the D.S.C. scan shows a distinct high endothermic peak with a maximum at 185°C. These observations indicate that the predominant structure after poling at these very high fields is phase I. The structure after poling is moreover oriented.

(b) D.S.C. and X-Ray Diffraction Data for Unoriented Films

The reflection and transmission x-ray scans for the poled unoriented films are shown in Fig. 6(a) and (b). The D.S.C. scans with a heating rate of 10°C/min are shown in Fig. 7. Essentially the same data was obtained if other heating rates were used. These data taken together also reveal structural and orientation changes occurring during poling.

1. In the D.S.C. scans the endothermic peak associated with the melting of phase II crystallites decreases and broadens with increasing poling field. At the same time a second endothermic peak, the size of which depends on the poling field, appears, with a maximum at 183°C. At the very highest poling field three separate endothermic peaks can be distinguished.
2. As before, the (020) reflection in the reflection mode decreases while the (020) reflection in the transmission mode is unchanged. At the same time the (010) reflection decreases both in the reflection and transmission scans, while the (200) reflection in the reflection mode is unchanged. This behavior is identical to the oriented films and can be explained by damage to phase II crystallites which are not oriented with the a-axis perpendicular to the film surface. These latter crystallites change to a polar structure, the intensity for (100) reflection being zero.
3. A new reflection appears (at $2\theta = 23.5^\circ$), the greatest intensity appearing for the films poled at 2.4×10^6 V/cm. This new reflection could not be indexed according to phase II, phase I or even phase III unit cells. The new reflection was not seen for the oriented sample so presumably it arises from chains not parallel to the film surface. Moreover it is seen only in the reflection mode not in the transmission mode, so it arises from oriented material.
4. For films poled at the highest fields, some phase I structure appears as indicated by the (110) reflection appearing as a shoulder on the phase II (110) reflection in the reflection mode. This is not seen in the transmission mode so it can be taken that the phase I formed at the highest poling field is oriented. The endothermic peak appearing only at the highest poling fields appears to be related to the appearance of the phase I structure.

(c) Mechanical and Electrical Measurements

Real and imaginary components of the elastic modulus, dielectric constant and piezoelectric stress and strain constants at temperatures from -70°C to 300°C can be obtained for poled polymer films using the Piezotron, manufactured by Toko Seiki Corporation. In this study only room temperature measurements were made. Although for the biaxially oriented films the thick poling electrodes could be stripped off leaving a clean surface, this could not be done for the unoriented films, possibly because of a greater surface roughness for the latter case. For this reason the piezoelectric constants were measured only for the oriented films.

Figure 8 shows the real component of the film elastic modulus at room temperature for the oriented films poled at fields up to $4 \times 10^6 \text{ V/cm}$. Figure 9 shows the real and imaginary components of the dielectric constant for both oriented and unoriented films. While the modulus appears slightly higher for the poled films, the real component of the dielectric constant both for the oriented and unoriented films shows a significant decrease. Both these effects could be attributed to field induced crystallization, i.e. a decrease in the amount of amorphous material.

Figure 10 shows the piezoelectric strain constant, d_{31} , for films poled at various poling field strengths and Figure 11 shows the piezoelectric stress constant, e_{31} . This data was obtained using a frequency of 3Hz. Very similar data was obtained using frequencies of 10Hz and 30Hz and is not shown here. As can be seen from Figures 10 and 11, although the piezoelectric stress and strain constants are not exactly equivalent, they both show essentially the same variation with poling field. At low poling fields piezoelectric activity is very low ($e_{31} < 2 \times 10^{-3} \text{ c/m}^2$ for $E_p < 1 \times 10^6 \text{ V/cm}$). For poling fields

between $1-2 \times 10^6$ V/cm the piezoelectric activity rises rapidly with poling field until a plateau region is observed $2.0-3.5 \times 10^6$ V/cm, with a value for $e_{31} \sim 14.5$. At the very highest poling field 4×10^6 V/cm a further increase in e_{31} of about 50%, to a value of 19.5×10^{-3} c/m² is observed. The piezoelectric strain constant shows similar features except that at the highest poling field only a slight upturn in the d_{31} value is observed.

DISCUSSION AND CONCLUSIONS

Previous studies^(6,7,8) have shown that films of phase II PVF₂ can be poled to give a large piezoelectric activity and this observation has been used to argue⁽⁵⁾ that the polarity of the crystal structure may not play a dominant role in the piezoelectric and pyroelectric phenomena observed in PVF₂ films. Other studies^(9,10) have shown that crystal structure changes occur after phase II films have been subject to corona discharge. Our data has shown that a large piezoelectric activity in phase II PVF₂ films can be induced by high poling fields at room temperature. The highest value obtained for d_{31} was 7.0 pc/N which compares with typical values obtained for oriented β -phase (using 1×10^6 V/cm and a poling temperature 80°C) of about 20 pc/N.

We have shown that a marked correlation between piezoelectric activity and crystal structure exists. At the low poling fields, when x-ray diffraction and D.S.C. data indicate that the PVF₂ film is predominantly phase II, the values for d_{31} and e_{31} are low. For poling fields between 1.0×10^6 and 2.0×10^6 V/cm, our x-ray diffraction data is consistent with the suggestion proposed by Davis and Broadhurst⁽¹⁰⁾ that a transformation to a polar phase with the same molecular packing as phase II occurs. Simultaneously the piezoelectric activity shows a marked increase with poling field in this region. The x-ray diffraction scans show very little change for films poled at field strengths from 2.0 to 3.5×10^6 V/cm. In this region the piezoelectric activity also seems to be independent of poling voltage. At the very highest poling field, a considerable amount of phase I structure is produced and simultaneously the piezoelectric activity shows a second marked increase.

The piezoelectric activity for the unoriented films has not been measured. X-ray diffraction and D.S.C. studies show a number of orientation and structural changes occur as a result of poling. In addition to the changes already discussed for the biaxially oriented film, some new structure appears to be formed giving rise to a reflection which cannot be indexed according to crystal structures already proposed. An endothermic peak in the D.S.C. associated with the production of this new structure can be observed. The molecular chain conformation of PVF_2 in the α -phase possesses a considerable dipole moment in the chain direction and it is possible that chain conformation changes, produced by the action of the poling field on chains perpendicular to the plane of the film, occur, to give the new structure. The new structure is certainly oriented since it is only observed in the x-ray scans taken in the reflection mode.

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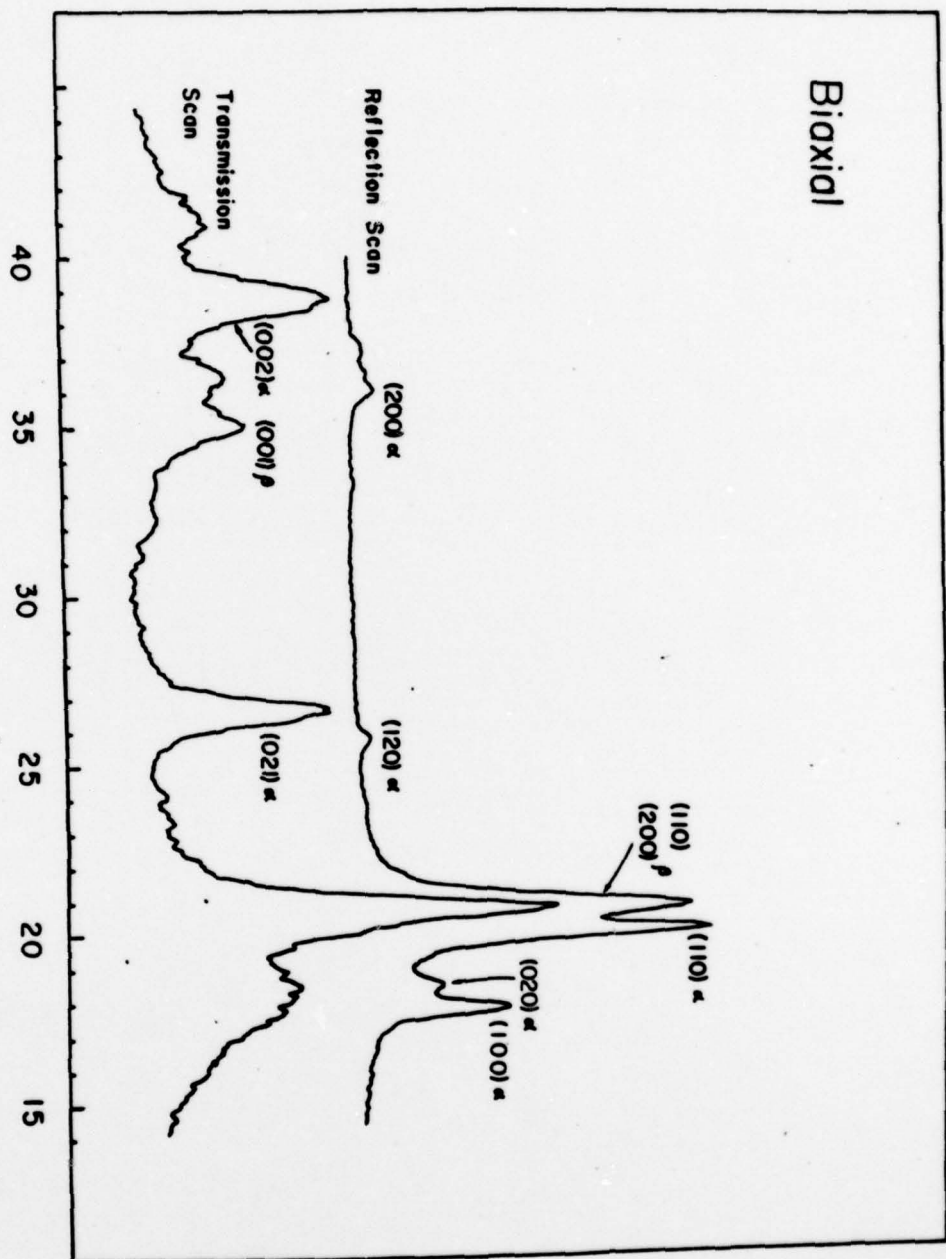
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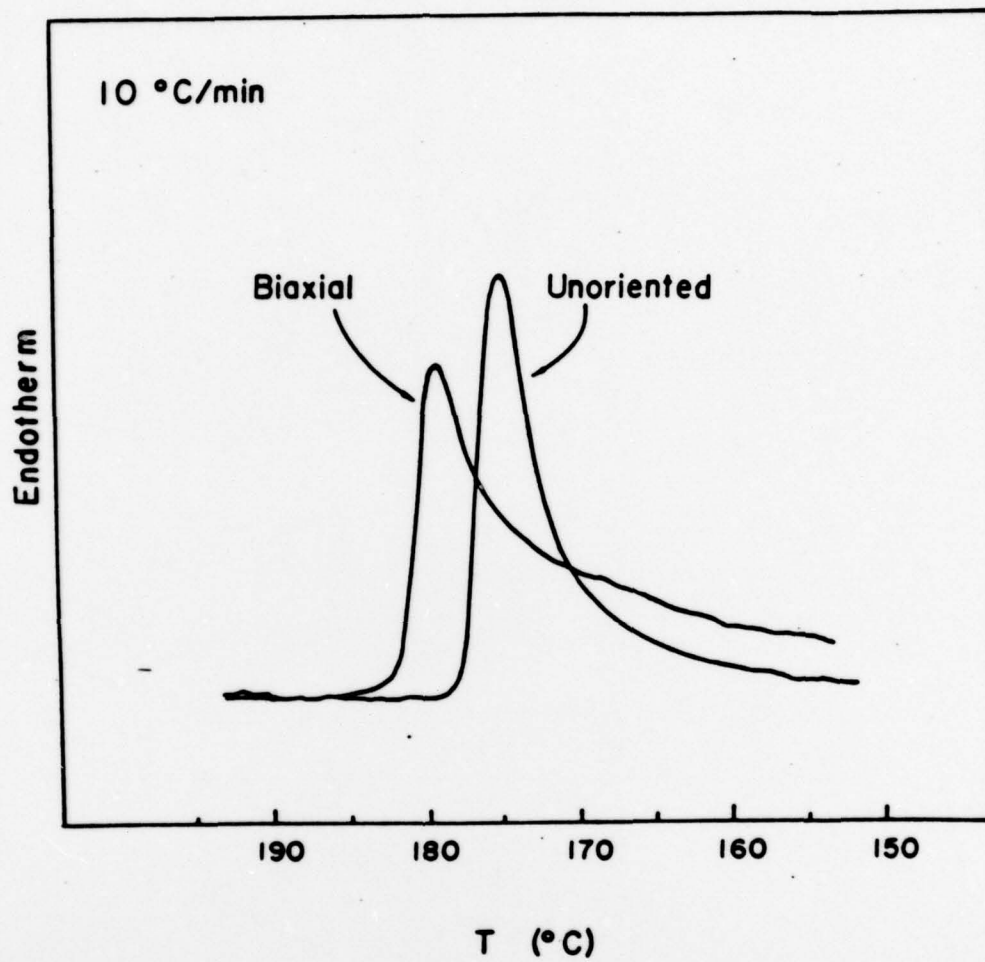
FIGURE CAPTIONS

- Figure 1 - X-ray diffraction scans for biaxially-oriented films.
- Figure 2 - D.S.C. scans for oriented and unoriented films.
- Figure 3 - X-ray diffraction scans for unoriented films.
- Figure 4 - X-ray diffraction scans taken in the reflection and transmission mode for poled biaxially-oriented films.
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- Figure 9 - Dielectric constant for poled films.
- Figure 10 - Piezoelectric strain constant for poled biaxially oriented films.
- Figure 11 - Piezoelectric stress constant for poled biaxially oriented films.

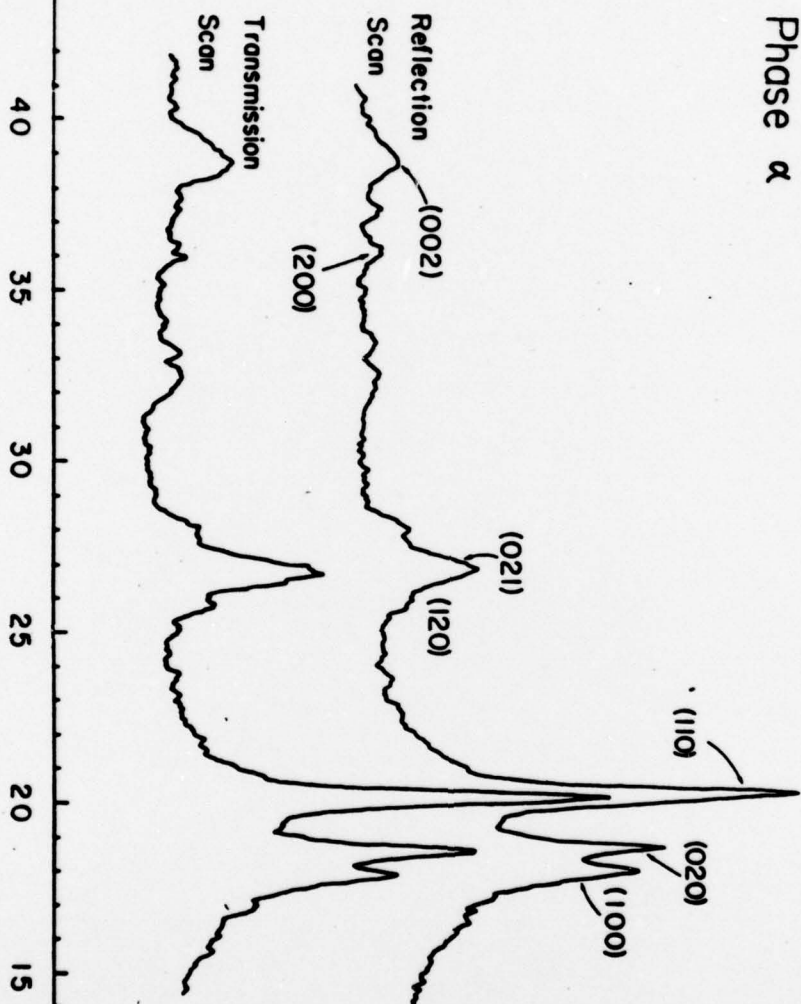
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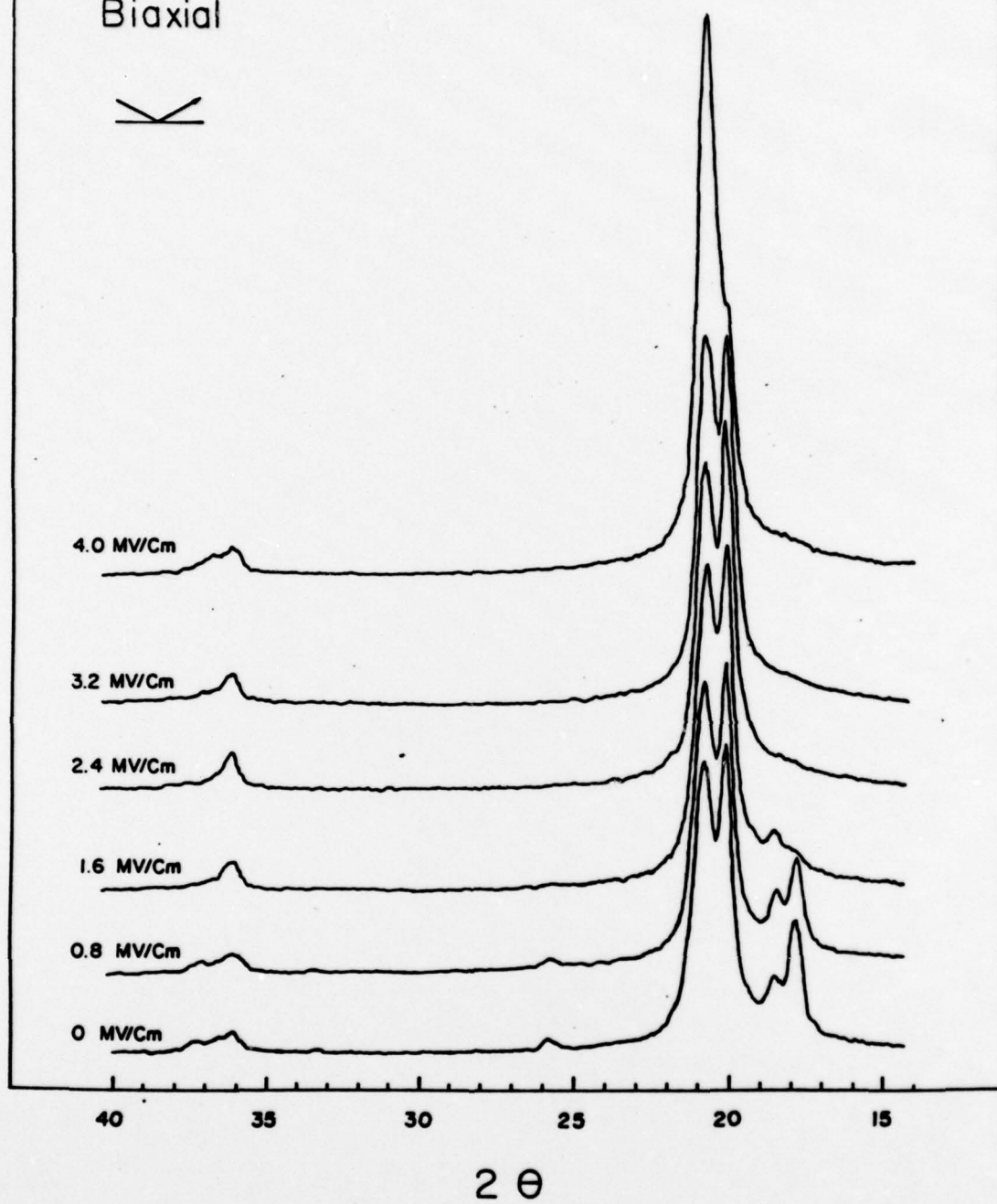


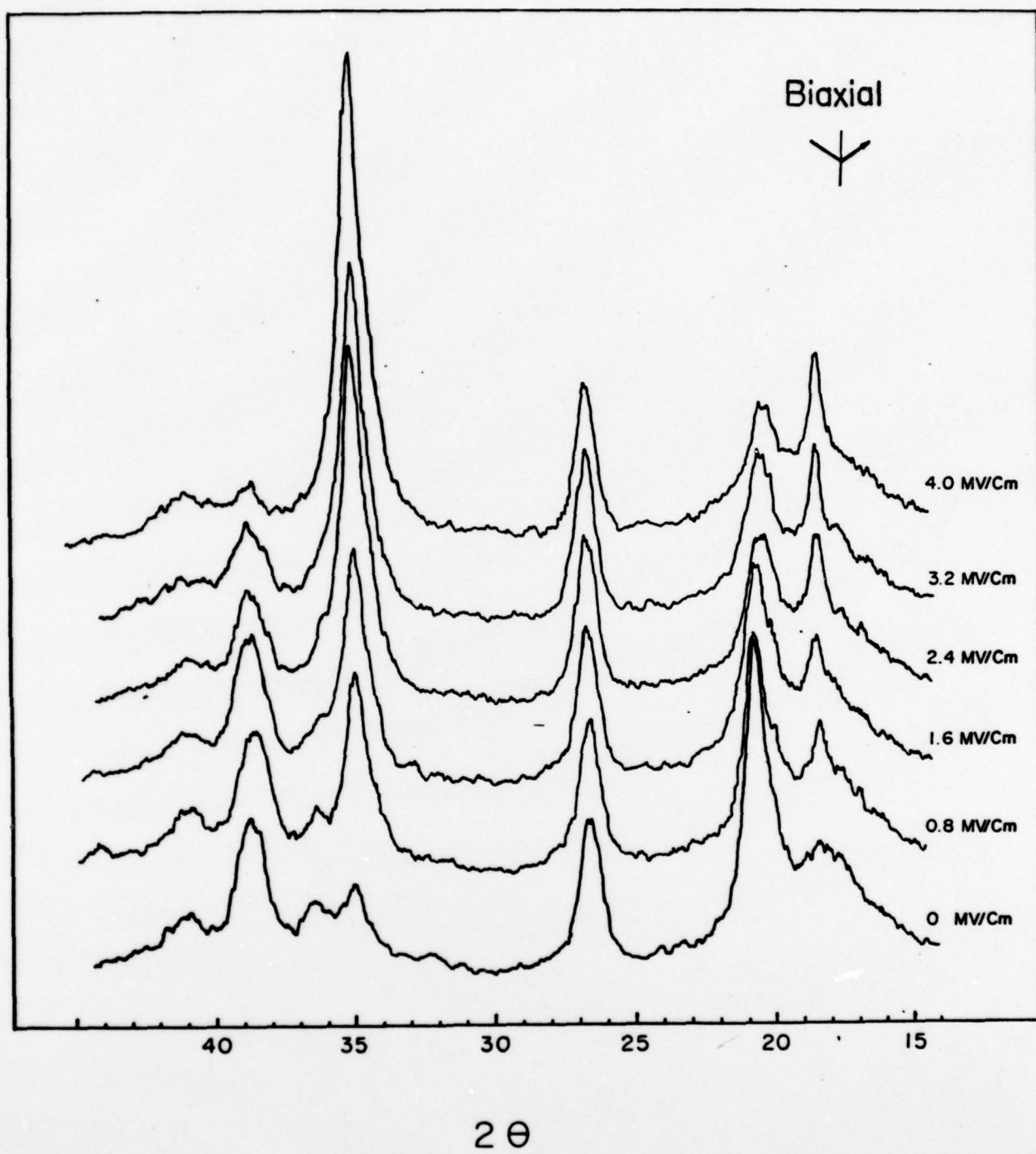
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Phase α

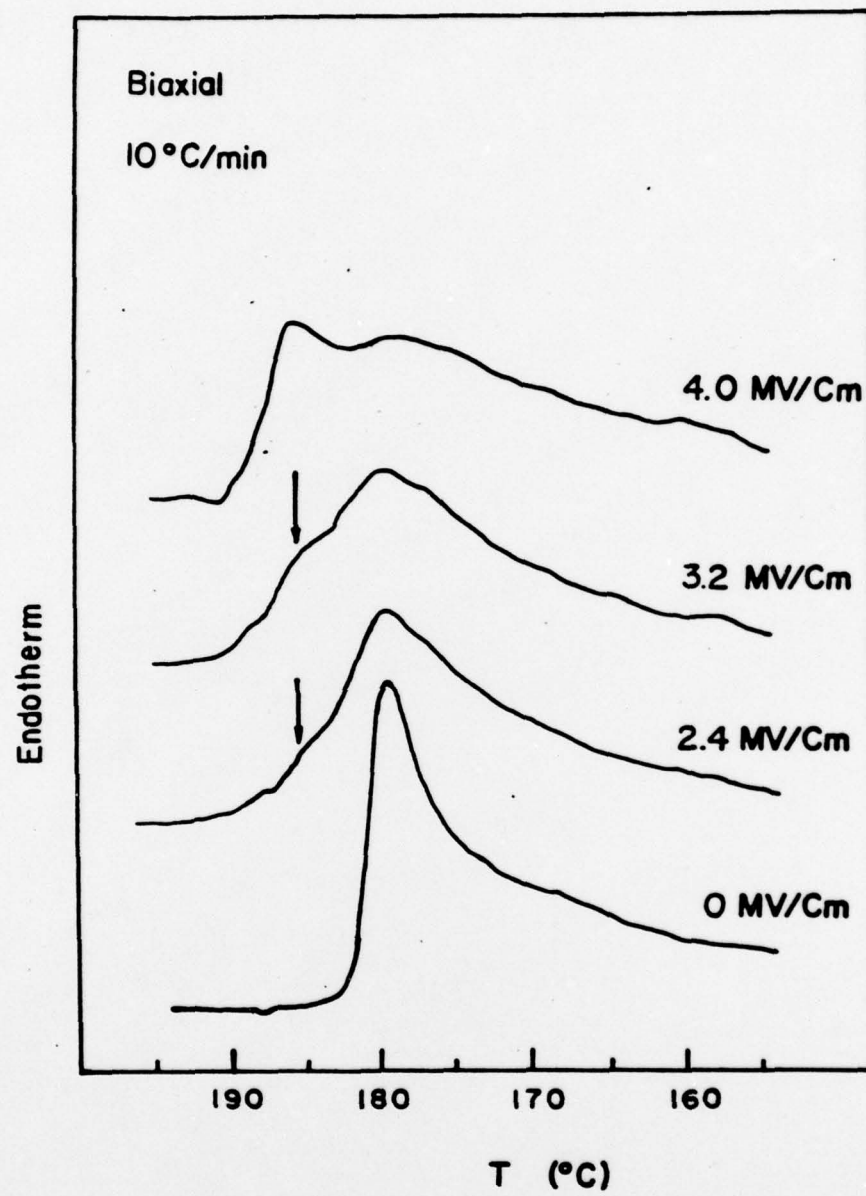


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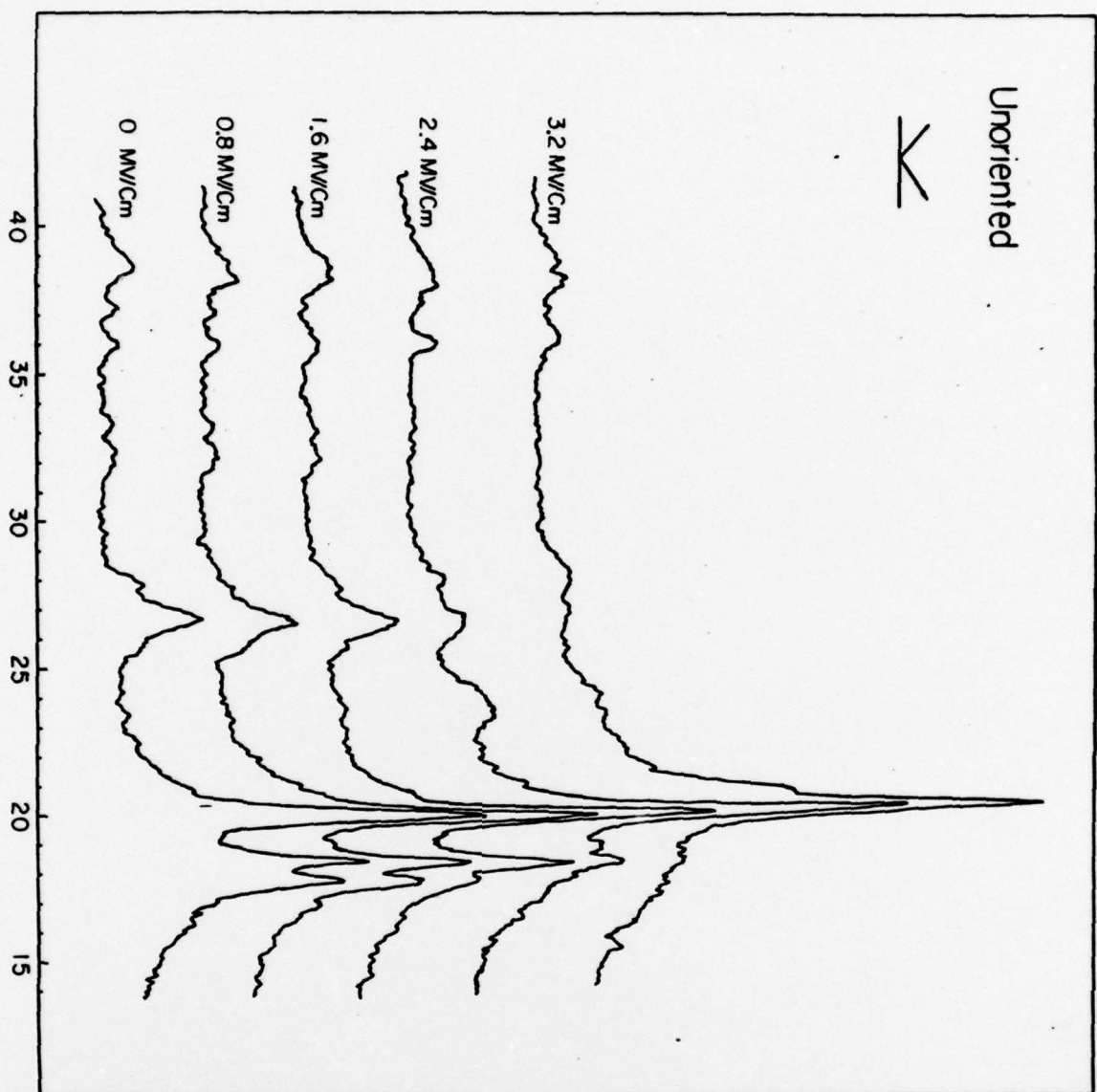
Biaxial







Unoriented



2θ

