AD-A083 650 RUTGERS - THE STATE UNIV PISCATAWAY NJ HIGH PRESSURE--ETC F/G 20/3
FERROELECTRIC HYSTERESIS EFFECTS IN POLY (VINYLIDENE FLUORIDE) --ETC(U)
APR 80 J I SCHEINBEIM, C H YOON, K D PAE N00014-75-C-0540
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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS ~~BEFORE~~ COMPLETING FORM

~~ORT NUMBER~~ chnical Report # 20

2. GOVT ACCESSION NO. AD A083 650

3. RECIPIENT'S CATALOG NUMBER

LE (and Subtitle)
RROELECTRIC HYSTERESIS EFFECTS IN POLY
INYLIDENE FLUORIDE) FILMS.

5. TYPE OF REPORT & PERIOD COVERED
Technical Report Interim

6. PERFORMING ORG. REPORT NUMBER

THOR(s)
I. Scheinbeim, C. H. Yoon, K. D. Pae ~~and~~
A. Newman

8. CONTRACT OR GRANT NUMBER(s)
(15) N00014-75-C-0540

RFORMING ORGANIZATION NAME AND ADDRESS
tgers University, High Pressure Research Lab.
d Dept. of Mechanics and Materials Science
llege of Engineering, Piscataway, NJ 08854

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
NR 356-564

NTROLLING OFFICE NAME AND ADDRESS
fice of Naval Research (Code 472)
lington, Virginia 22217

12. REPORT DATE
(11) 1 Apri[illegible]980

13. NUMBER OF PAGES

NITORING AGENCY ~~NAME & ADDRESS~~(if different from Controlling Office)

LEVEL II

15. SECURITY CLASS. (of this report)
(12) 25

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

STRIBUTION STATEMENT (of this Report)
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STRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

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PPLEMENTARY NOTES

Y WORDS (Continue on reverse side if necessary and identify by block number)
ly(vinylidene fluoride), Ferroelectric, Hysteresis, Phase IV

STRACT (Continue on reverse side if necessary and identify by block number)

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0540

Task No. NR 356-564

TECHNICAL REPORT NO. 20

FERROELECTRIC HYSTERESIS EFFECTS IN POLY (VINYLIDENE FLUORIDE) FILMS

by

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Prepared for Publication

in the

Journal of Applied Physics

High Pressure Materials Research Laboratory
Department of Mechanics and Materials Science
College of Engineering
Rutgers University
P. O. Box 909
Piscataway, New Jersey 08854

April 1, 1980

80 4 24 055

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J. I. Scheinbeim, C. H. Yoon, K. D. Pae and B. A. Newman
High Pressure Materials Research Laboratory
Department of Mechanics and Materials Science
College of Engineering, Rutgers University
P. O. Box 909, Piscataway, New Jersey 08854

Abstract

Investigations of the piezoelectric response of biaxially oriented poly(vinylidene fluoride) films subjected to a series of static positive and negative poling fields produces a hysteresis curve for d_{31} and e_{31} showing the ferroelectric character of phase IV. Examination of changes in the crystalline regions, using differential scanning calorimetry and x-ray methods, of films cycled (statically) through large positive and negative poling fields, provides insight into the switching mechanisms of both phase I and phase IV. The experimental results show a cyclic broadening and narrowing of the endothermic melting peaks as the film polarization is switched. Cyclic changes in the intensities of the phase I (110)(200) and phase II (or phase IV) (100), (020), and (110) reflections are also observed.

Introduction

Previous investigations of the piezoelectric activity of poled poly(vinylidene fluoride) (PVF_2) films indicate that this activity is directly related to field induced changes in the crystalline regions of this semicrystalline polymer.[1] These field induced changes include crystal phase transitions from nonpolar to polar forms or from less polar to more polar forms and reorientation of the crystalline regions.[1-5] It is also known that the polarization responsible for the observed piezoelectric and pyroelectric activity is switchable, i.e. that the direction of film polarization can be reversed by application of a reversed poling field of sufficient magnitude.[6-8]

Studies of the time development of film polarization show that it does not occur immediately upon application of the poling field (for conventional two-terminal poling) but exhibits a time dependence which is characterized by a rapid increase during the first minutes of poling, followed by a slow increase occurring over many hours.[9-11] This time development of film polarization is, of course, a function of both poling field and temperature.[8] In a recent study we have also shown that the time dependence of the polarization is related to the time dependence of the field induced phase transitions and that the transition rates are dependent on initial crystallite orientation with respect to the field direction.[12] Because of this time dependence, examinations of the (ferroelectric) switching behavior of PVF_2 films by conventional A.C. techniques using, for example, a 60 Hz alternating field may not be of much value. This is emphasized by the early work of Buchman[8] who observed switching times of the order of several minutes at temperatures as high as 150°C.

In addition to these difficulties, A.C. methods measure the polarization under the applied field and therefore include contributions from film conductivity and from the amorphous regions. Both of these contributions would affect the shape of the P-E curve.

In order to minimize these problems and to allow as to gain further insights into the effects of polarization reversal on crystallite structure and morphology, we conducted a series of static switching experiments. By poling the films for one hour at each of the forward or subsequent reversed poling fields, we were able to examine hysteresis effects in film polarization (as indicated by the piezoelectric response, d^*_{31} and e^*_{31}). Using x-ray methods and differential scanning calorimetry (D.S.C.) we studied reversible changes occurring in the crystalline regions of the films.

Experimental

Biaxially oriented, capacitor grade Kureha PVF_2 25 micron films were electroded with silver paste. The samples were then subjected to different poling histories, i.e. some specific set of forward and reversed poling fields.

The poling histories of different samples is shown in Table 1. Samples 1 and 2 were simply subjected to single poling fields of 0.6 MV/cm and 1.4 MV/cm respectively. Samples 3 to 7 were subjected to the same poling field of 1.4 MV/cm and then different fields in the reverse direction from -0.8 MV/cm to -2.8 MV/cm. Samples 8 to 17 were subjected to the same field of 1.4 MV/cm, then a reversed field of -2.8 MV/cm, followed by a third poling field in the initial direction which varied from 0.4 MV/cm to 2.8 MV/cm. Samples 14 to 16 were subjected to four successive fields; an initial positive field of 1.4 MV/cm, a second negative field of 2.8 MV/cm, a positive third field of 2.8 MV/cm, and final negative fields of -1.2 MV/cm, -1.4 MV/cm and -2.8 MV/cm.

Samples with slightly different histories were also poled, in order to allow accurate interpolation between data points. These points are shown on some of the later figures but for reasons of brevity are not explicitly labelled. The poling history of the labelled samples is given in detail because they were found to be representative of observed cyclic behavior.

The poling times at each poling field was one hour and the poling temperature was 23°C. Previous investigation in our laboratory has shown that most of the crystallographic changes produced by poling at this temperature occur within one hour for the poling fields used. A conventional, two terminal, poling technique was used: the output of a high voltage D.C. supply was connected across the sample. Poling was performed under vacuum with a pressure $\sim 10^{-5}$ torr. Piezoelectric measurements (d^*_{31} and e^*_{31}) were performed at 3 Hz using a Toyo Seiki Piezotron.

After completion of the electrical measurements, the electrode material was removed and wide angle x-ray diffraction scans (using CuKα radiation) were taken in reflection mode. After completion of the x-ray studies, the melting behavior of the samples subjected to different poling histories was determined with a Perkin-Elmer DSC I-B differential scanning calorimeter, using a heating rate of 10°C/min.

Results

1) Electrical Measurements

The real and imaginary components of the piezoelectric strain constant, d^*_{31}, for samples subjected to different poling histories are shown in Figures 1a and 1b. The numbered data points have the poling histories shown in Table 1.

Along the line from sample 1 to sample 2 (path $1 \rightarrow 2$) d_{31} increases with increasing poling field as previously observed.[1] The two points corresponding to sample 2 (which are connected by a dashed line) indicate that d_{31} is unchanged if no reversed poling field is applied. Along the path 2→7, sample 2 is subjected to increasingly negative (reversed) poling fields, and d'_{31} decreases from +4.5 $\frac{pC}{N}$ to zero and then reverses its sign. The field necessary to drive d'_{31} and, presumably, the remnant film polarization to zero is -0.96 MV/cm. When the reversed field reaches -2.8 MV/cm, $d'_{31} = -5.8$ pC/N.

Application of subsequent positive poling fields produces points on the path 7→13 which again shows d'_{31} going to zero when the switching field reaches 0.96 MV/cm. A final reversed field produces the path 13→16.

The hysteresis like behavior shown for d'_{31} and d''_{31} in Figure 1 is also apparent in Figures 2a and 2b, which show the components of the piezoelectric stress constant, e'_{31} and e''_{31}, for the same samples. Both the d^*_{31} and e^*_{31} data show saturation effects at poling fields of ~±2 MV/cm. This saturation in the piezoelectric response with increasing poling field was previously observed and has been shown to hold for poling fields up to ~3.5 MV/cm; at higher poling fields, both d_{31} and e_{31} show further increase.[1] The apparent saturation value for d'_{31} is 6 $\frac{pC}{N}$ and for e'_{31} is 16 x 10^{-3} C/m^2.

2) X-Ray Measurements

The wide angle x-ray diffraction scans (in reflection mode) of PVF_2 films subjected to different poling histories are shown over a limited range of Bragg angle ($16° \leq 2\theta \leq 24°$) in Figures 3a and 3b. The diffraction scans show the variation in diffracted intensity with poling history for the most important reflections: (100), (020), and (110) from phase II, and (110) (200) from phase I. These scans show evidence of a field induced phase transition from phase II to another phase with the same unit cell dimensions as II but with different structure factors. This has been reported previously by several workers and the new structure termed polar phase II or phase II*. Since the structure is crystallographically distinct from phase II here it is termed phase IV.

It is important to remember that the observed diffracted intensity (in reflection mode) is only due to crystallographic planes parallel to the film surface. Therefore, all the crystallites contributing to the observed reflections, whether phase II, phase IV, or phase I, have their c axes (chain axis) in the plane of the film, since the c axis is parallel to the (hoo), (oko), and (hko) planes in all these polymorphic forms of PVF_2. Those phase II crystallites contributing to the (100) reflection have (100) planes parallel to the film surface and a-axis perpendicular to the film surface: The (100) structure factor for phase IV is zero.[3] Those phase II or phase IV crystallites contributing to the (020) reflection have (020) planes parallel to the film surface and a axes parallel to the film surface. The a axes of the phase II or phase IV crystallites contributing to the (110) reflection make an angle of 63° with the film surface.

The reason for emphasizing the a axis orientation of the phase II or phase IV crystals contributing to the observed reflections is that in both structures, the TGTG' molecular conformation has a large dipole moment component parallel or antiparallel to the a axis. As pointed out by Davis, et al,[3] this large moment normal to the chain axis (c axis) allows for large interaction energies with the applied field.

For the phase I (110)(200) reflection, those crystallites contributing to the (200) intensity have b axes parallel to the film surface while those crystallites contributing to the (110) reflection have their b axes at an angle of 60° to the film surface. The molecular conformation in phase I is all trans with the CF_2 dipoles along b.

In Figures 3a and 3b, the numbers used to label the diffractometer scans correspond to samples subjected to the poling histories shown in Table 1. If the same symbol is used for more than one scan (for example, the dotted line used for samples 2 and 4), the scans were identical within experimental error (~±2%).

The diffractometer scan of sample 1, poled at 0.6 MV/cm showed no change from that of the unpoled sample. The scan from sample 2, poled at +1.4 MV/cm shows the previously reported changes in x-ray intensity consistent with the phase transition from phase II to phase IV[3]: The (100) reflection decreased significantly but the (200) reflection (which is not shown) increased slightly. This indicates that most phase II crystals with a perpendicular to the film surface have transformed to phase IV. A much smaller decrease in the (020) reflection is also observed indicating that some phase II crystals with a parallel to the film surface have changed their orientation and are no longer in diffracting position. Since the crystal structure of phase II is antipolar, these crystallites have probably transformed to phase IV or phase III. The (020) structure factors of phase II and phase IV are the same.[3] The intensities of the phase II (110) reflection and the phase I (110) (200) reflection are unchanged.

If sample 2 is now subjected to a reversed poling (switching) field of -0.8 MV/cm (sample 3), the (100) reflection increases slightly and the (020) reflection returns to its original (unpoled) value. If sample 2 is subjected to a switching field of -1.4 MV/cm (sample 4), no change in the diffractometer scan is observed. Further increase in the reverse poling field to -2.8 MV/cm (sample 7) results in the disappearance of both the (100) and (020) reflections and increases in the (110) and (110)(200) reflections. The (110) structure factor of phase IV is ~20% greater than that of phase II.[3] The data indicates that many of the phase II crystals contributing to the observed (110) reflection have now transformed to phase IV. The increase in the phase I (110) reflection is consistent with a field induced reorientation of some phase I crystals. The actual change in (110) intensity may be greater than the observed change since it is possible that phase I crystals originally contributing to the (200) reflection (dipole moment perpendicular to the applied field) have moved out of diffracting position.

In Figure 3b, sample 7, which has been subjected to poling fields of +1.4 MV/cm and then -2.8 MV/cm is now considered as the baseline with which to compare changes produced by the application of additional switching fields. If a field of +0.4 MV/cm is now applied to sample 7, the only observed change (sample 8) is a decrease in the phase I (110)(200) reflection. Increasing the switching field to +1.2 MV/cm (sample 10) produces a large decrease in the (110)(200) and (110) reflections and a small increase in the (100) and (020) reflections. A further increase in switching field applied to sample 7 to +2.8 MV/cm (sample 13) increases the (110)(200) and (110) intensities and the (100) and (020) reflections disappear: The (110)(200) and (110) intensities are lower than those of sample 7. Finally (sample 16), a switching field of -2.8 MV/cm applied to sample 13 causes an increase in both the (110)(200) reflection and the (110) reflection. The (110)(200) intensity of sample 16 is greater than that of sample 7, while the (110) reflection of sample 16 has the same intensity as sample 7: Sample 7 was subjected to poling fields of +1.4 MV/cm and -2.8 MV/cm. Sample 16 was subjected to poling fields of +1.4 MV/cm, -2.8 MV/cm, +2.8 MV/cm, and -2.8 MV/cm. i.e. the magnitude and direction of the last switching field applied to these samples was the same.

3) DSC Measurements

The melting behavior of samples subjected to different poling histories (see Table 1) is shown in Figure 4: equal weights of each sample were used. The melting behavior of sample 1 (E_p = +0.6 MV/cm) and the unpoled sample are the same and are shown at the bottom of the figure. The DSC scans of samples 2→7, 7→17, and 13→16 are placed in three separate groups, since each group represents an additional reversal of poling field direction applied to the samples. The after melting baselines of the scans in each group are matched as the heat capacities of the samples are assumed to be the same in the liquid state.

The melting endotherm of sample 2 (E_p = +1.4 MV/cm) has a smaller peak height than that of the unpoled sample and has a small, but significant, high temperature tail after the large melting peak. Application of a switching field of -0.8 MV/cm to sample 2 (sample 3) increased the height of the melting peak and removed the high temperature tail. If the switching field applied to sample 2 is increased to -2.8 MV/cm (sample 7) the peak height of the melting endotherm again decreases and the endotherm has developed a large high temperature shoulder.

In the second group of endotherms (7-12) sample 7, subjected to poling fields of +1.4 MV/cm and -2.8 MV/cm, is used as a reference. Application of increasingly larger switching fields to sample 7 (+0.8 MV/cm, sample 9; +1.4 MV/cm, sample 11) increases the height of the endothermic peak and decreases the size of the high temperature shoulder. The change in melting behavior again reverses for switching fields of +2.0 MV/cm (sample 12) and +2.8 MV/cm (sample 13); the peak height decreases and the high temperature shoulder increases.

The last reversed poling cycle (samples 13-16) produces a similar cyclic behavior in the shape of the endothermic melting peak. As the switching field is increased, first an increase in peak height and a decrease in the high temperature shoulder occurs, followed at higher switching fields by a decrease in peak height and an increase in the high temperature shoulder.

The temperature at which the peak in the melting endotherm occurs in samples 1-14 is 178°C. In samples 15 and 16 it has decreased to ~177°C.

Discussion and Conclusions

In previous investigations, we examined the relationship between poling field magnitude, crystalline changes observed in x-ray diffraction and D.S.C. studies and piezoelectric response (a measure of remnant film polarization) of the biaxially oriented PVF_2 films used in the present study. These investigations have shown that the phase II crystals undergo a field induced phase transition to a polar crystal form now termed phase IV and that the amount of material converted to phase IV was directly related to the observed increase in the piezoelectric constants d_{31} and e_{31}. The piezoelectric activity is related to the remnant polarization of the poled films which is a function of the number and orientation of the polar crystallites present.

In the present study, we examined the reversibility or switching properties of the film polarization by subjecting the films to a series of static switching fields and determining the piezoelectric response as a function of switching field magnitude and direction. Figures 1 and 2 show that as the switching field is cycled from positive to negative values, a hysteresis loop for d_{31} and e_{31} (and presumably, film polarization) is obtained. A saturation value of 6 pC/N for d'_{31} and 16×10^{-3} C/m^2 for e'_{31} is observed. Both d_{31} and e_{31} go to zero when the reversing field reaches ±0.96 MV/cm. Although the results of these measurements show the ferroelectric nature of these PVF_2 films, they were not unexpected, since previous work conducted using different techniques showed similar ferroelectric behavior.[6-8] The primary purpose of this work was to examine the changes in the crystalline regions of the films after the film polarization was switched.

An initial poling field of +1.4 MV/cm was shown to convert most of the phase II crystals contributing to the (100) reflection to phase IV. As the field is cycled from large negative to large positive values, the (100) intensity exhibits small but significant cyclic changes in intensity. This suggests that the reversal of polarization for phase IV crystallites may occur in two steps: a transformation back to phase II, followed by another transformation to phase IV. Each of these steps would lower the interaction energy of the crystals with the applied field. The (020) reflection also exhibits some cyclic behavior. Whether or not the proposed two-step transformation actually occurs, we believe that the cyclic changes in intensity indicates that the phase IV crystals exhibit ferroelectric behavior, i.e. that the direction of polarization of phase IV crystals can be switched. This is also apparent from the cyclic behavior observed for the intensity of the (110) reflection.

The phase I crystals contributing to the observed (110)(200) reflection also exhibit cyclic switching behavior; however, two switching mechanisms probably occur. Previous studies[13] of unoriented phase I films poled at 1 MV/cm at 23°C showed high piezoelectric activity, but subsequent x-ray studies indicated that only 180° switching had occurred. In this study, no change in the (110)(200) intensity is observed for poling histories of +1.4 MV/cm and +1.4 MV/cm followed by -1.4 MV/cm, indicating 180° flipping. As the field is cycled through higher values, the (110)(200) intensity exhibits cyclic behavior consistent with a new switching behavior. Most probably, the 60° flipping mechanism proposed by Kepler and Anderson[5] on the basis of the pseudo-hexagonal phase I structure, takes place.

The cyclic broadening and narrowing of the endothermic melting peak which occurs for samples subjected to successive positive and negative fields is also a new phenomena. This cyclic behavior would be consistent with the two-step switching mechanism suggested for phase IV, if we associate the phase IV crystals with the broad melting peak and the phase II crystals with the narrow melting peak.

As the data indicates, both phase IV and phase I crystals can be switched by the application of appropriate poling fields. Phase I exhibits two field dependent switching mechanisms. Phase IV may have a two-step switching mechanism, $II \rightarrow IV^{+} \rightarrow II \rightarrow IV^{-}$, which would be consistent with the cyclic behavior observed in both the x-ray and DSC data. Further investigations of the phase IV switching mechanisms are needed to provide a more complete understanding of the observed behavior.

Acknowledgment

The authors gratefully acknowledge the financial support of the Office of Naval Research (Contract No. N00014-75-C-0540) for these research studies.

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Figure Captions

Table I - A list of the poling field history for each of the numbered samples. Each field was applied for one hour at 23°C.

Figures 1a and 1b - The in phase (d'_{31}) and quadrature (d''_{31}) components of the piezoelectric strain coefficient $d^*_{31} = d'_{31} - i\, d''_{31}$ of samples subjected to the poling field cycles listed in Table I.

Figures 2a and 2b - The in phase (e'_{31}) and quadrature (d''_{31}) components of the piezoelectric stress coefficient $e^*_{31} = e'_{31} - i\, e''_{31}$ of samples subjected to the poling field cycles listed in Table I.

Figures 3a and 3b - Wide angle diffractometer scans of samples subjected to the poling field cycles listed in Table I.

Figure 4 - The melting behavior of samples subjected to the poling field cycles listed in Table I.

TABLE I

A List of the Poling Field History for each of the Numbered Samples. Each Field was Applied for One Hour at 23°C.

Sample No.	Poling Fields Applied to Sample (MV/cm)
1	+0.6
2	+1.4
3	+1.4, -0.8
4	+1.4, -1.4
5	+1.4, -1.6
6	+1.4, -2.0
7	+1.4, -2.8
8	+1.4, -2.8, +0.4
9	+1.4, -2.8, +0.8
10	+1.4, -2.8, +1.2
11	+1.4, -2.8, +1.4
12	+1.4, -2.8, +2.0
13	+1.4, -2.8, +2.8
14	+1.4, -2.8, +2.8, -1.2
15	+1.4, -2.8, +2.8, -1.4
16	+1.4, -2.8, +2.8, -2.8

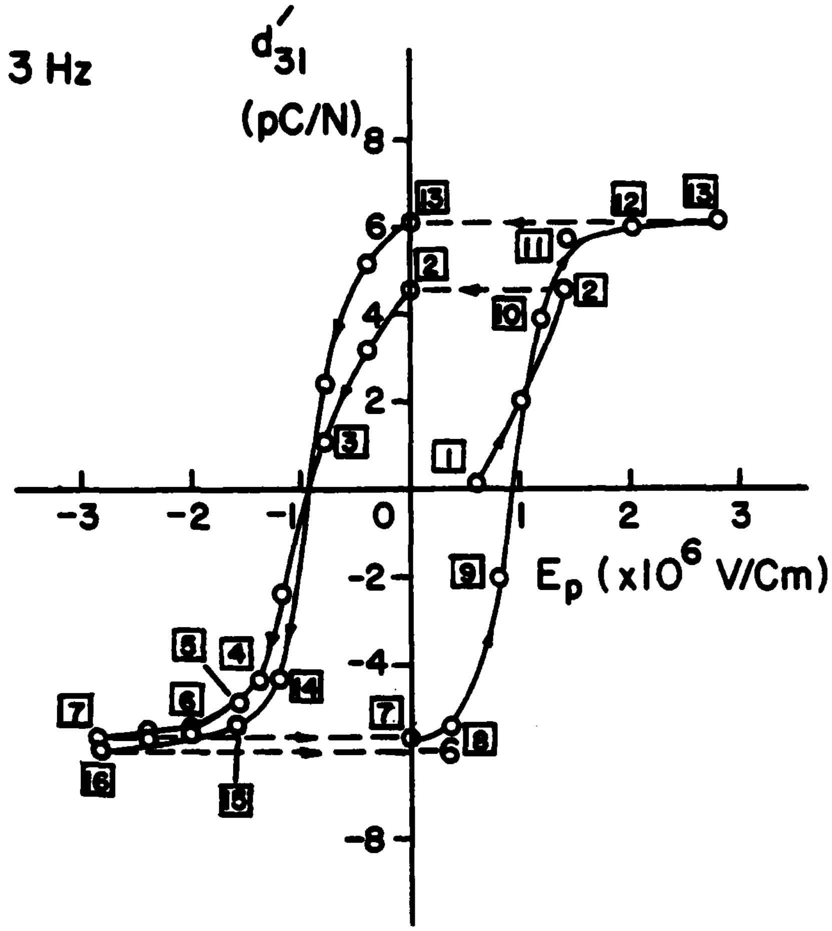
3 Hz
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Fig 1a

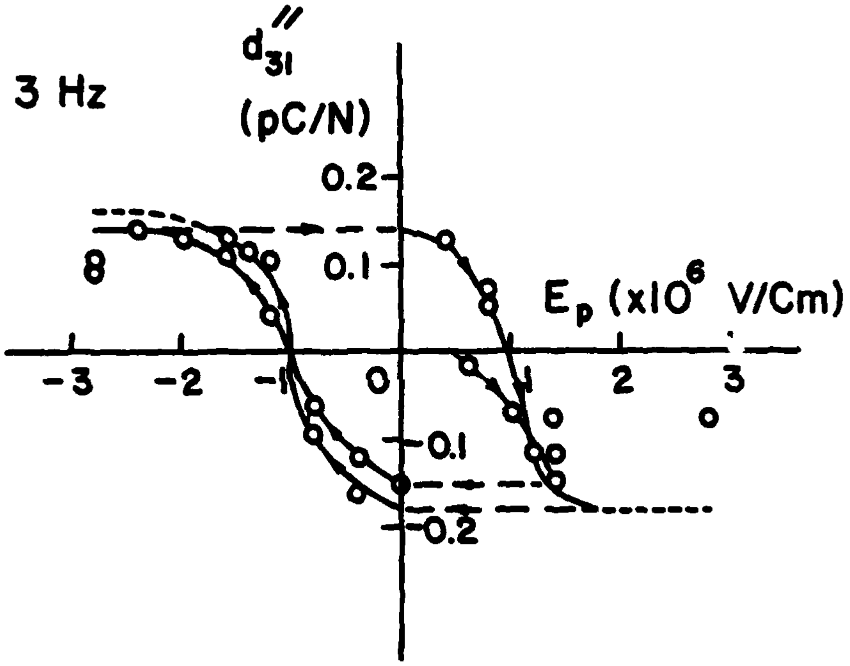

Fig 16

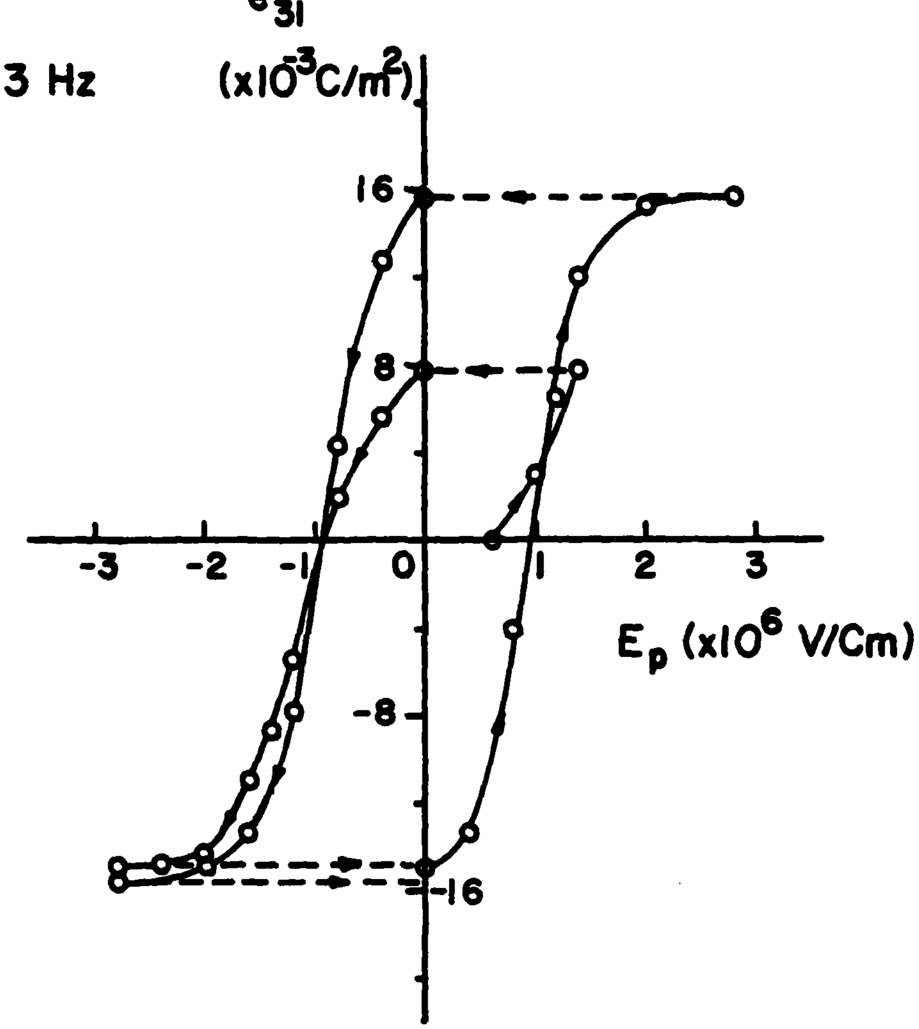

Fig 2a

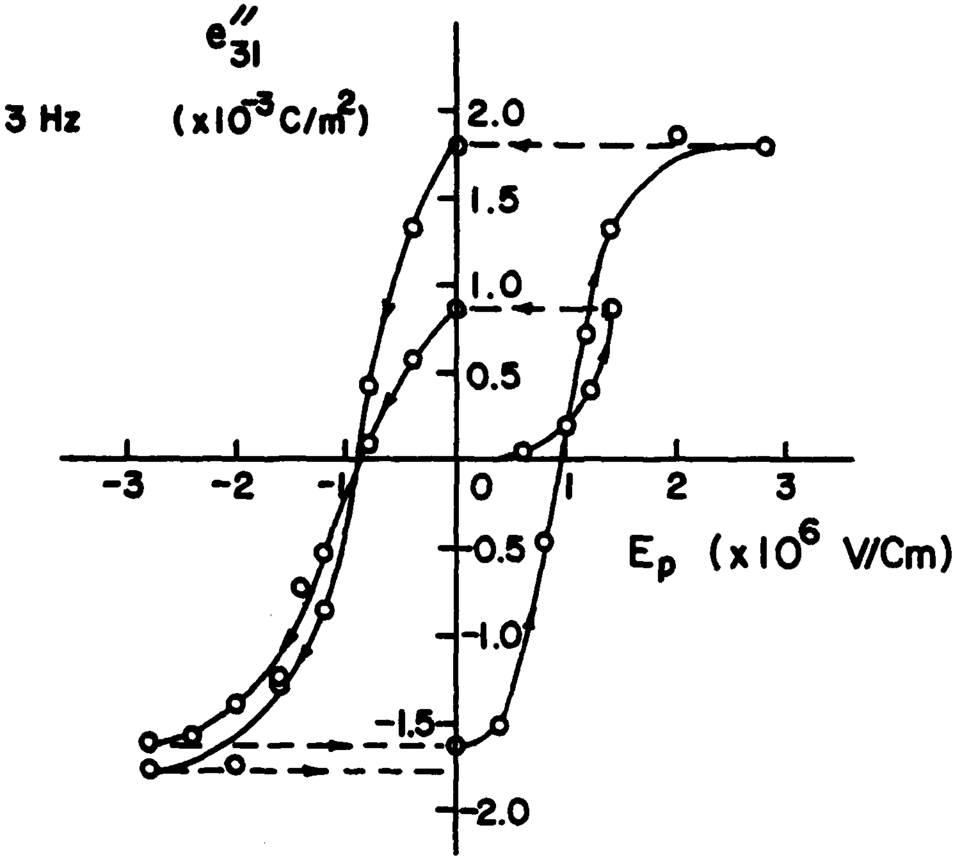

Fig 2b

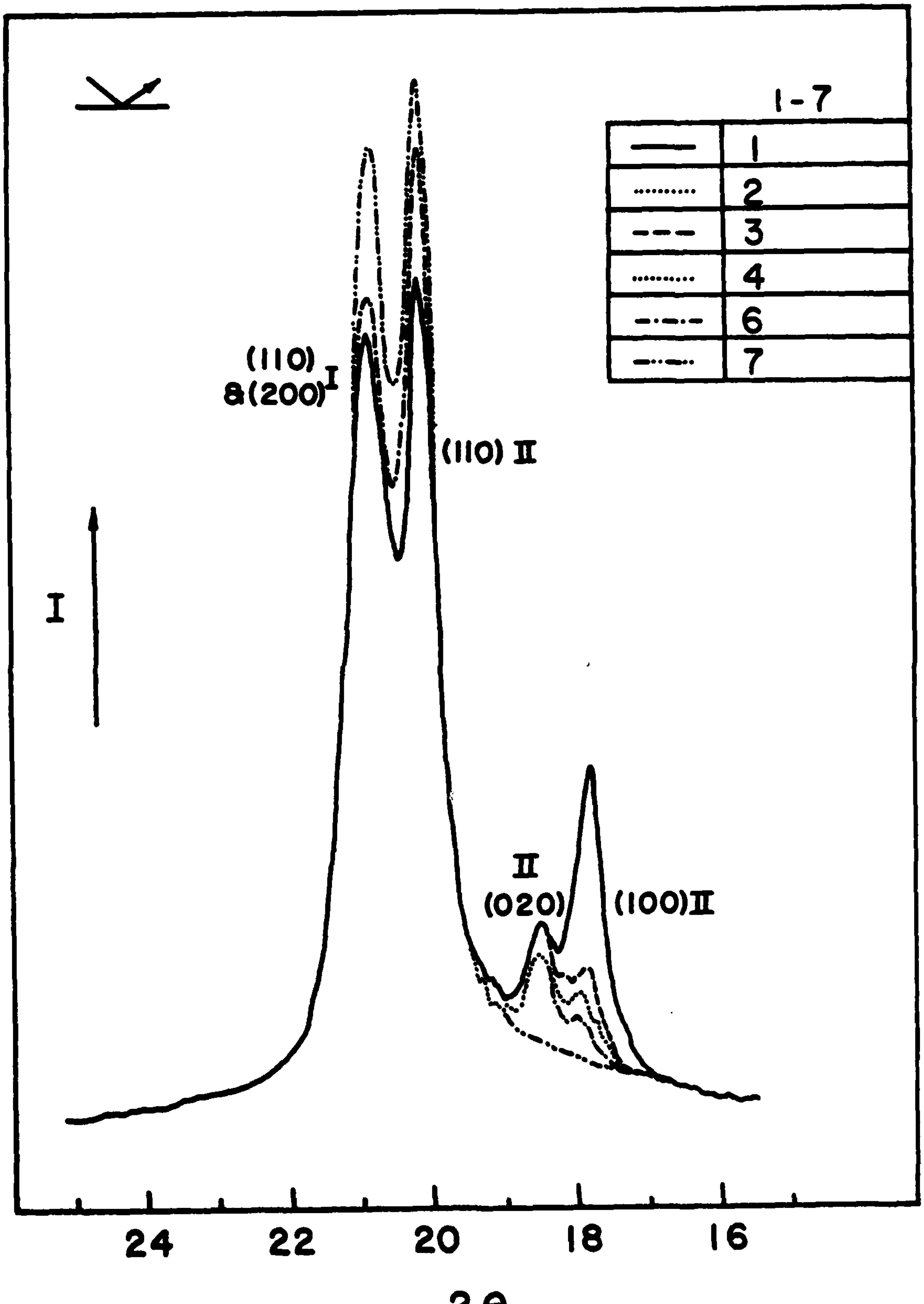

Fig 3a

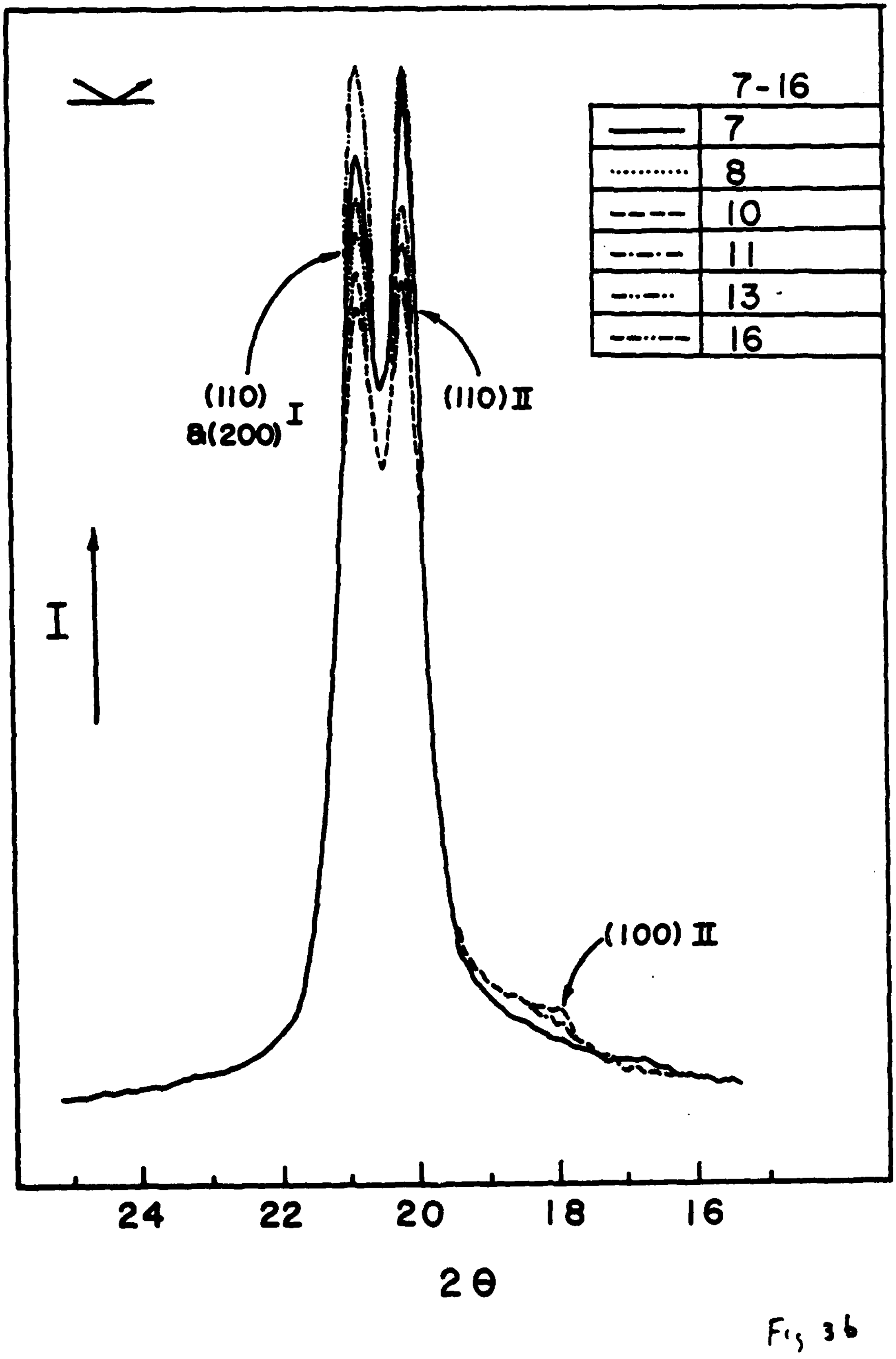

Fig 3b

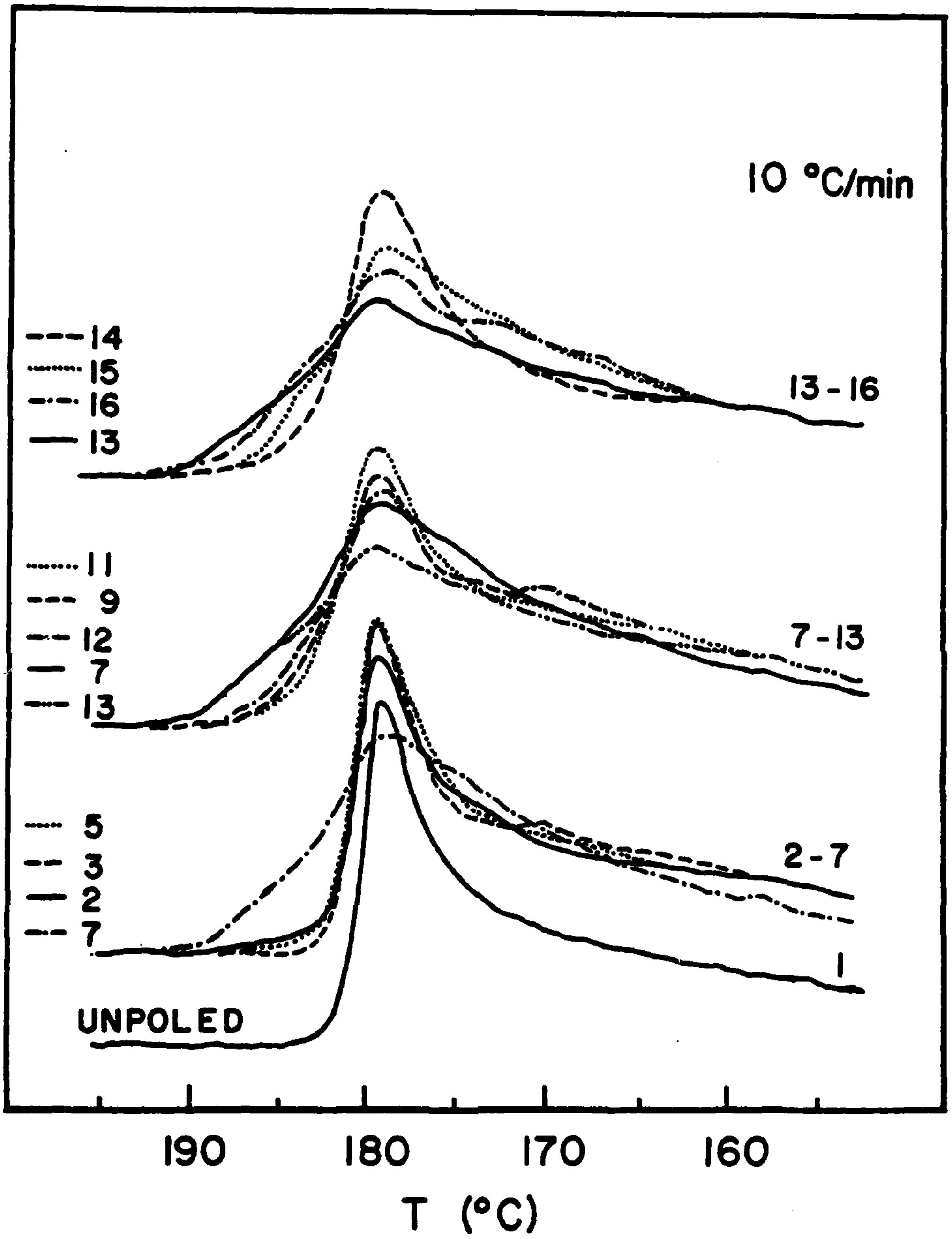
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Fig 4

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