

AD-A081 821

RUTGERS - THE STATE UNIV PISCATAWAY NJ HIGH PRESSURE--ETC F/6 11/9
THE POLING TIME DEPENDENCE OF THE FIELD INDUCED PHASE TRANSITION--ETC(U)
MAR 80 J I SCHEINBEIM, C H YOON, K D PAE N00014-75-C-0540
UNCLASSIFIED TR-16 NL

[OF]
[500 50]



END
DATE
FILMED
4-80
DTIC

ADA081821

5 (12) LEVEL II

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #16	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) THE POLING TIME DEPENDENCE OF THE FIELD INDUCED PHASE TRANSITION AND PIEZOELECTRIC RESPONSE OF POLY(VINYLDENE FLUORIDE) FILMS		5. TYPE OF REPORT & PERIOD COVERED Technical Report Interim
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) J.I. Scheinbeim, C.H. Yoon, K.D. Pae and B.A. Newman		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0540
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rutgers University, High Pressure Research Lab & Dept. of Mechanics & Materials Science, College of Engineering, Piscataway, NJ 08854		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-564
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research (Code 472) Arlington, Virginia 22217		12. REPORT DATE March 1, 1980
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. Reproduction in whole or in part is permitted for any purpose of the United States Government.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) High Pressure, Poly(vinylidene fluoride), Piezoelectric		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) We have examined the poling time dependence of the field induced phase transi- tion (from phase II to polar phase II) of biaxially oriented poly(vinylidene fluoride) films by x-ray methods. These results were compared with the poling time dependence of the piezoelectric response (d_{31} and e_{31}) determined by using a Piezotron Model U (Toyo Seiki, Tokyo). The piezoelectric response shows an initial rapid increase with poling time followed by a slow increase as the poling time increases. The x-ray results show that the field induced phase transition is time dependent, and occurs first for those crystallites with		

DTIC
ELECTE
S MAR 12 1980 D
A

DD FORM 1473

EDITION OF 1 NOV 68 IS OBSOLETE
S/N 0102-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

2 Jul 81 2 Aug 81

their a axes perpendicular to the film surface. Crystallites with a in the plane of the film transform at a much slower rate. The data indicate that the poling time dependence of d_{31} and e_{31} (and, presumably, film polarization) are dependent on the transition rates.

d₃₁ 31

e₃₁ 31

OFFICE OF NAVAL RESEARCH

Contract ¹⁵ N00014-75-C-0540

Task No. NR 356-564

9, TECHNICAL REPORT NO. 16

THE POLING TIME DEPENDENCE OF THE FIELD
INDUCED PHASE TRANSITION AND PIEZOELECTRIC
RESPONSE OF POLY(VINYLIDENE FLUORIDE) FILMS.

by

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

Prepared for Publication

in the

Journal of Polymer Science

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

11, 2 Mar 1980 12 3

Accession For	
NTIS GRA&I	☒
DDC TAB	☐
Unannounced	☐
Justification	
By _____	
Distribution/ _____	
Availability Codes	
Dist. H	Avail and/or Special

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

80 3 11 006

THE POLING TIME DEPENDENCE OF THE FIELD INDUCED PHASE TRANSITION
AND PIEZOELECTRIC RESPONSE OF POLY(VINYLIDENE FLUORIDE) FILMS

by

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

Synopsis

We have examined the poling time dependence of the field induced phase transition (from phase II to polar phase II) of biaxially oriented poly(vinylidene fluoride) films by x-ray methods. These results were compared with the poling time dependence of the piezoelectric response (d_{31} and e_{31}) determined using a Piezotron Model U (Toyo Seiki, Tokyo). The piezoelectric response shows an initial rapid increase with poling time followed by a slow increase as the poling time increases. The x-ray results show that the field induced phase transition is time dependent, and occurs first for those crystallites with their a axes perpendicular to the film surface. Crystallites with a in the plane of the film transform at a much slower rate. The data indicate that the poling time dependence of d_{31} and e_{31} (and, presumably, film polarization) are dependent on the transition rates.

THE POLING TIME DEPENDENCE OF THE FIELD INDUCED PHASE TRANSITION
AND PIEZOELECTRIC RESPONSE OF POLY(VINYLDENE FLUORIDE) FILMS

by

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

We have examined the poling time dependence of the field induced phase transition (from phase II to polar phase II) of biaxially oriented poly(vinylidene fluoride) films by x-ray methods. These results were compared with the poling time dependence of the piezoelectric response (d_{31} and e_{31}) determined using a Piezotron Model U (Toyo Seiki, Tokyo). The piezoelectric response shows an initial rapid increase with poling time followed by a slow increase as the poling time increases. The x-ray results show that the field induced phase transition is time dependent, and occurs first for those crystallites with their a axes perpendicular to the film surface. Crystallites with a in the plane of the film transform at a much slower rate. The data indicate that the poling time dependence of d_{31} and e_{31} (and, presumably, film polarization) are dependent on the transition rates.

Introduction

Previous investigations of the dependence of the polarization of poled poly(vinylidene fluoride) (PVF₂) films on poling time¹⁻⁷ indicate that the polarization occurs in two stages. First, a rapid increase in polarization occurs, followed by a slowly increasing polarization. Some investigators reported that the fast increase occurred within

seconds, while others reported that it occurred within minutes of the application of the poling field. Most agreed that the slow increase occurred over a time period of hours. Other data implied that the rate of increase in polarization depended on poling temperature, with the maximum possible film polarization dependent only on poling field.

Although the poling time dependence of the film polarization has been well established, the mechanisms responsible for the initial rapid increase or the following slow increase have not been determined. However, it has been suggested that the polarization is nonuniform and an increase in the uniformity of polarization may be responsible for the slow increase.^{3,8}

In this laboratory, we have been investigating the mechanisms responsible for the observed polarization of PVF_2 films, using piezoelectric activity as a measure of film polarization. This was done by examining the changes occurring in the crystalline regions of the poled films using x-ray diffraction methods and by attempting to correlate the crystallographic changes with changes in piezoelectric response. Previous work⁹⁻¹¹ has shown that the poling of biaxially oriented PVF_2 films containing primarily the nonpolar phase II polymorphic crystal form produces a phase transition from phase II to a polar crystal form called polar phase II (or II*). It has been suggested that this oriented polar phase II crystalline material is responsible for the film polarization. Using d_{31} and e_{31} , the piezoelectric strain and stress constants respectively, as measures

of film polarization, we found a strong correlation between the amount of material converted from phase II to polar phase II and film polarization for films poled for several hours.¹¹ We, therefore, decided to investigate the possibility of a poling time dependence for the previously observed phase transition and, if such a time dependence existed, attempt to correlate it with the time dependent changes in film polarization.

Experimental

Biaxially oriented, 25 micron thick samples of capacitor grade Kureha PVF₂ film were electroded with silver paste. The samples were then poled at various poling times (6 sec, 30 sec, 1 min, 3 min, 10 min, 30 min, 1 hr and 2 hrs). The poling field used was 2×10^6 V/cm and the poling temperature was 23°C. In this study, a conventional, two-terminal, poling technique was used. The output of a high voltage D.C. supply (5 KV) was connected through a switch across the sample. Poling was done under vacuum, with a pressure $\sim 10^{-5}$ torr. Piezoelectric measurements were performed using a Toyo Seiki Piezotron.

After the electrical measurements were completed, the electrode material was removed and wide angle x-ray diffraction scans (using CuK_α radiation) were taken in reflection and transmission mode.

Results and Discussion

(a) Electrical Measurements

A plot of the complex piezoelectric stress constant, e_{31}^* versus poling time is shown in Fig. 1. e_{31}^* exhibits the expected poling time dependence: a fast increase occurring during the first several seconds

followed by a much slower increase as the poling time increases to two hours. In Fig. 2, the complex piezoelectric stress constants, d_{31}^* , obtained using different poling times are plotted. A similar time dependence can be observed. The data indicate that both e_{31}^* and d_{31}^* reach ~80% of their final (2 hour) value in less than 10 seconds.

(b) X-Ray Measurements

The wide angle x-ray diffraction scans (reflection and transmission) of PVF₂ films poled for different times are shown over a limited range of Bragg angle (16°-24°) in Figs. 3 and 4. The diffraction scans show the variation in diffracted intensity with poling time for the most important reflections (100), (020) and (110) from phase II and the (110), (200) reflection from phase I. It is important to realize that a comparison of reflection and transmission scans permit a comparison of the response of different crystallites (with different orientations to the film surface) to poling. The reflection scans show the previously reported changes in x-ray reflections consistent with the phase transition from phase II to polar phase II⁽⁹⁻¹¹⁾. The (100) reflection decreased but the (200) reflection, (which is not shown here) increased slightly. In Fig. 3, it can be seen also that changes occurring in those crystallites contributing to the (100) reflection (a axis perpendicular to the film surface) and those crystallites contributing to the (020) reflection (b axis perpendicular to the film surface) occur at different rates. The peak height of the (100) reflection decreased to ~1/3 of its initial value during the first 6 seconds of poling,

while the (020) reflection has undergone no significant change. At the end of 30 seconds of poling, the peak height of the (100) reflection is $\sim 1/5$ its initial value, while the peak height of the (020) reflection is $\sim 3/4$ its initial value. Time dependent changes in intensity can also be observed in the (110) reflection and the phase I (110) (200) reflection.

The x-ray diffraction scans taken in transmission mode (shown in Fig. 4) exhibit much smaller changes when compared to the reflection scans. Since the time dependent changes were quite small, only the scans for the unpoled sample and the sample poled for two hours are included. The most significant changes are; a small decrease in the (100) reflection, a larger increase in the (020) reflection, and a decrease in the phase I (110) (200) reflection. The time dependence of these changes could not be accurately determined. The reflection scans show that crystallites with their a axes perpendicular to the film surface transform rapidly to polar phase II as evidenced by the large decrease in intensity of the (100) reflection during the first six seconds of poling. Those crystallites with their b axes perpendicular to the film surface transform at a much slower rate, as evidenced by the slower change in intensity of the (020) reflection. In fact, after six seconds of poling, no significant change in the intensity of the (020) reflection has occurred. With these facts in mind, it appears quite plausible to assume that the rapid increase in film polarization (as suggested by the rapid increase in d_{31} and e_{31} shown

in Fig. 1 and Fig. 2) is due to the phase transition from phase II to polar phase II, for crystals with a perpendicular (or close to perpendicular) to the film surface. The slower increase in polarization during the next several hours of poling would be due to the completion of the phase transformation for these crystals and the much slower rate of transformation for crystals whose a axes are at some larger angle with respect to the normal to the film surface: For the biaxially oriented films used, the c axes are in the plane of the film.

The phase II crystal structure (see Fig. 5) has two chains in the unit cell. One of the chains has a large dipole moment component parallel to a and the other (symmetry related) chain has a large dipole moment component antiparallel to a. It has been suggested that the phase transition from phase II to polar phase II occurs by a 180° field-induced rotation of one of the chains, producing the structure shown in Fig. 6.^{9,10} A simultaneous translation of the chain along c has also been suggested.⁹

If one accepts the theory that the phase transition is caused by the interaction between the applied poling field and the molecular dipoles, and given the data presented here which shows a time dependent phase transformation dependent on crystallite orientation, then the previously described relationship between crystallite orientation and phase transformation rate may be explained.

The driving force for the time dependent transformation would be

the interaction energy ($u = -\underline{\mu} \cdot \underline{E}$) of the poling field ($\underline{E}$) with the component of the molecular dipole moment perpendicular to the chain axis ($\underline{\mu}$). The change in molecular interaction energy occurring during the phase transition (assuming 180° rotation of one molecule) is $u = 2\mu E$ for molecules in crystals with $\underline{a}$ perpendicular to the film surface. (since $\underline{E}$ is perpendicular to the film surface). As the angle, ϕ , between $\underline{a}$ and the normal to the film surface increases u decreases and the driving force for the phase transition decreases (reaching a minimum when $\phi = 90^\circ$) implying that crystallites with $\phi > 0$ may not transform as rapidly. However, for crystallites with $\phi \sim 90^\circ$, a 180° rotation of one chain would produce a very small energy decrease and for $\phi = 90^\circ$, no energy decrease at all. That these crystals do transform is evidenced by the decrease in the (020) reflection in reflection mode. One may therefore propose a different transition mechanism for these crystals; 90° rotation of both chains in the unit cell into the field direction. The change in interaction energy counting both chains in the unit cell would be $2\mu E$ for both cases: $\phi = 0$ and $\phi = 90^\circ$. However, the barrier for 180° rotation of one chain and for the cooperative 90° rotation of both chains in the unit cell should be very different.

The possibility for 90° rotation of both chains is indicated by the decrease in intensity of the (020) reflection in reflection mode and its increase in transmission mode: a pole figure analysis of the (020) reflection is needed to firmly establish that 90° rotation can occur.

The availability of two distinct transition mechanisms would account for the rapid decrease in the (100) reflection ($\phi = 0$) and the much slower decrease in the (020) reflection ($\phi = 90^\circ$) if the barrier

for 180° rotation of one chain were less than the barrier for 90° cooperative rotation of both chains in the unit cell. This simple picture of the rate dependence of the phase transition on crystallite orientation needs further investigation. Future temperature dependent studies of the poling time dependence of changes in the (100) and (020) poles (pole figure analysis) should provide an indication of the allowed transformations (180° , 90° , etc.) and information on the activation energy of the transformations.

Acknowledgment

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

References

- (1) N. Murayama, T. Oikawa, T. Kaito, and K. Nakamura, J. Polym. Sci., Polym. Phys. Ed., 13, 1033 (1975).
- (2) D. Naegle and D. Y. Yoon, Appl. Phys. Lett. 33, 132 (1978).
- (3) H. Sussner and K. Dransfield, J. Polym. Sci., Polym. Phys. Ed., 16, 529 (1978).
- (4) E. Fukada and M. Oshika, Nat. Bur. Stads. (U.S.) Interagency Rep., 75-760 (1975).
- (5) J. E. McKinney and G. T. Davis, Polymer Preprints, 271 (1978).
- (6) R. I. Shufford, A. F. Wilde, J. J. Ricca and G. R. Thomas, Polym. Eng. Sci., 16, 25 (1975).
- (7) P. D. Southgate, Appl. Phys. Lett. 28, 250 (1976).
- (8) G. W. Day, C. A. Hamilton, R. L. Peterson, R. J. Phelan, and L. O. Mullen, Appl. Phys. Lett. 24, 458 (1974).
- (9) D. K. Das-Gupta and K. Doughty, Appl. Phys. Lett. 31, 585 (1977).
- (10) G. T. Davis, J. E. McKinney, M. G. Broadhurst and S. C. Roth, J. Appl. Phys. 49, 10 (1978).
- (11) B. A. Newman, C. H. Yoon, K. D. Pae and J. I. Scheinbeim, J. Appl. Phys. 50, 6095 (1979).

FIGURE CAPTIONS

Figure 1 - A plot of the complex piezoelectric stress constant e_{31}^* versus poling time ($E_p = 2 \times 10^6$ V/cm, $T_p = 23^\circ\text{C}$)

Figure 2 - A plot of the complex piezoelectric strain constant d_{31}^* versus poling time ($E_p = 2 \times 10^6$ V/cm, $T_p = 23^\circ\text{C}$)

Figure 3 - Wide-angle x-ray diffractometer scans of samples poled for different poling times (reflection mode)

Figure 4 - Wide-angle x-ray diffractometer scans of unpoled sample and sample poled for two hours (transmission mode)

Figure 5 - C axis projection of phase II unit cell

Figure 6 - C axis projection of polar phase II unit cell

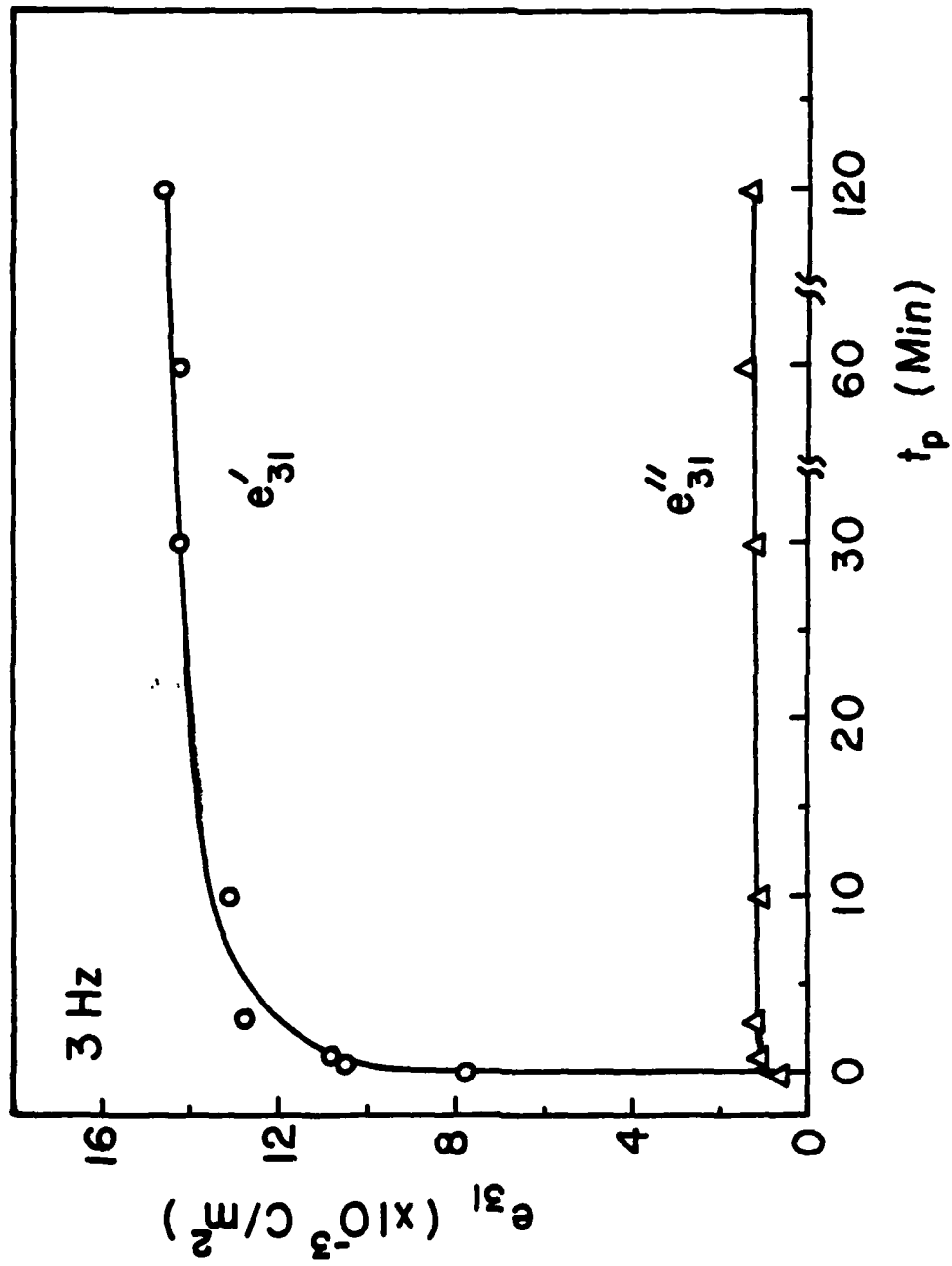
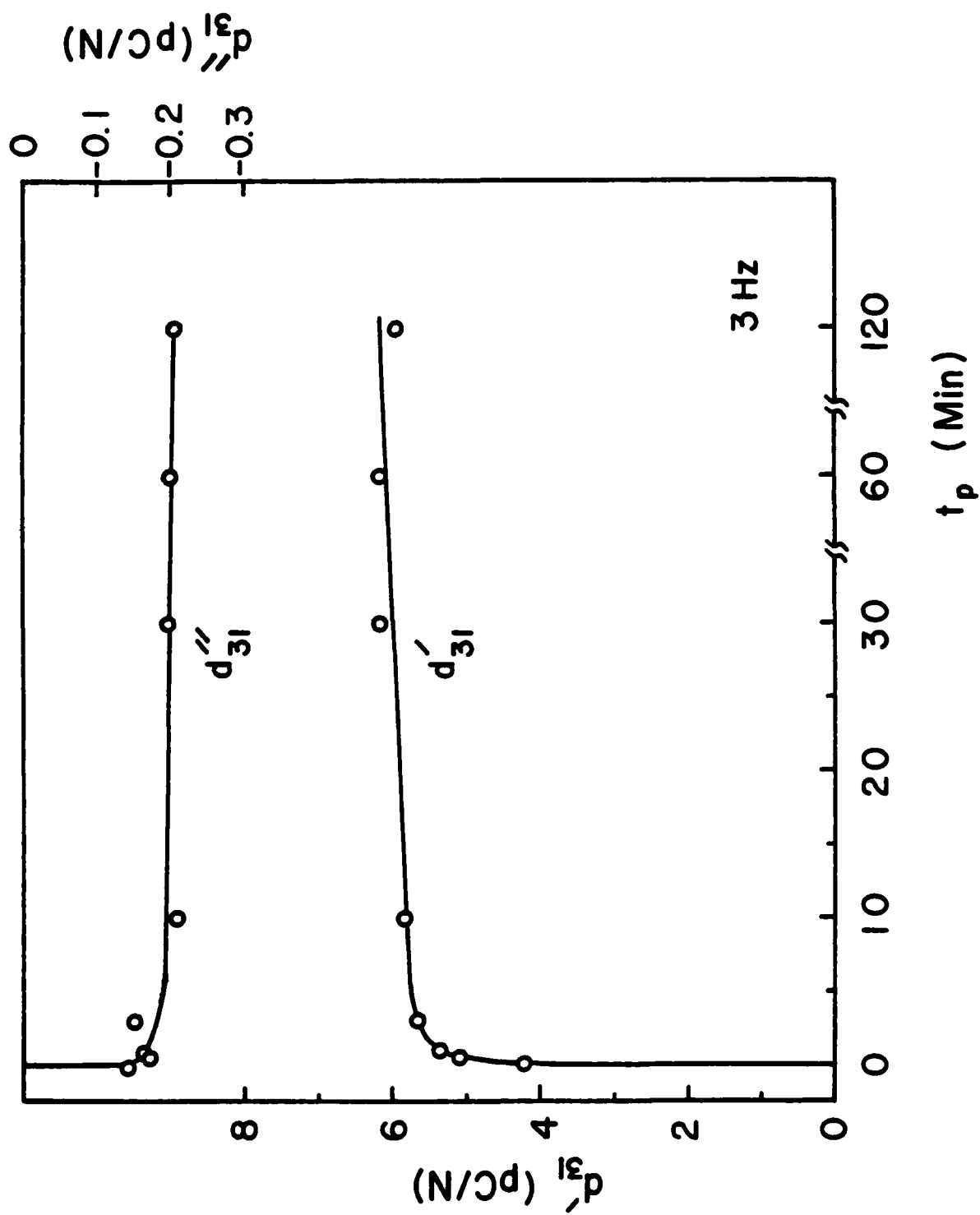
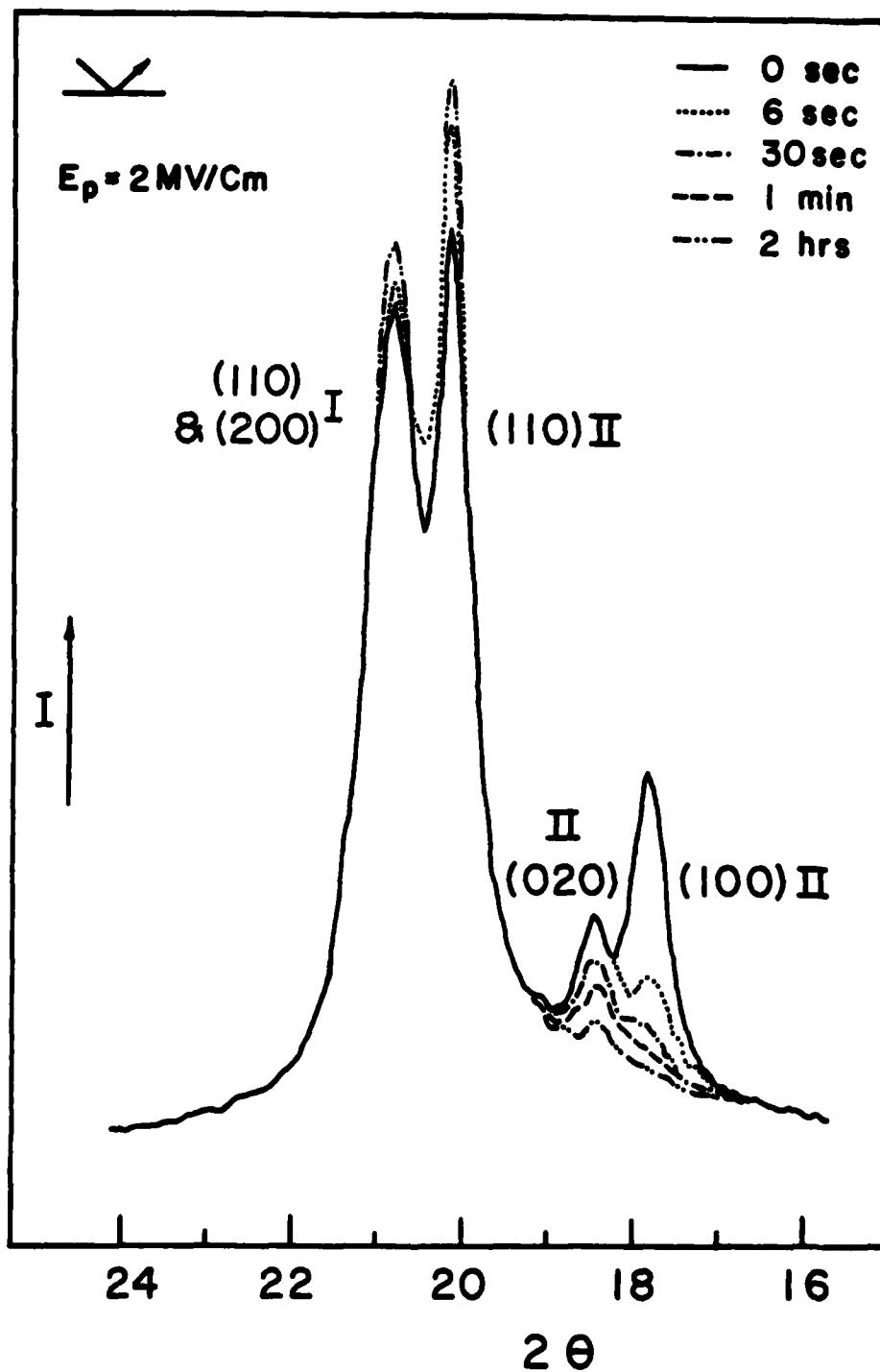
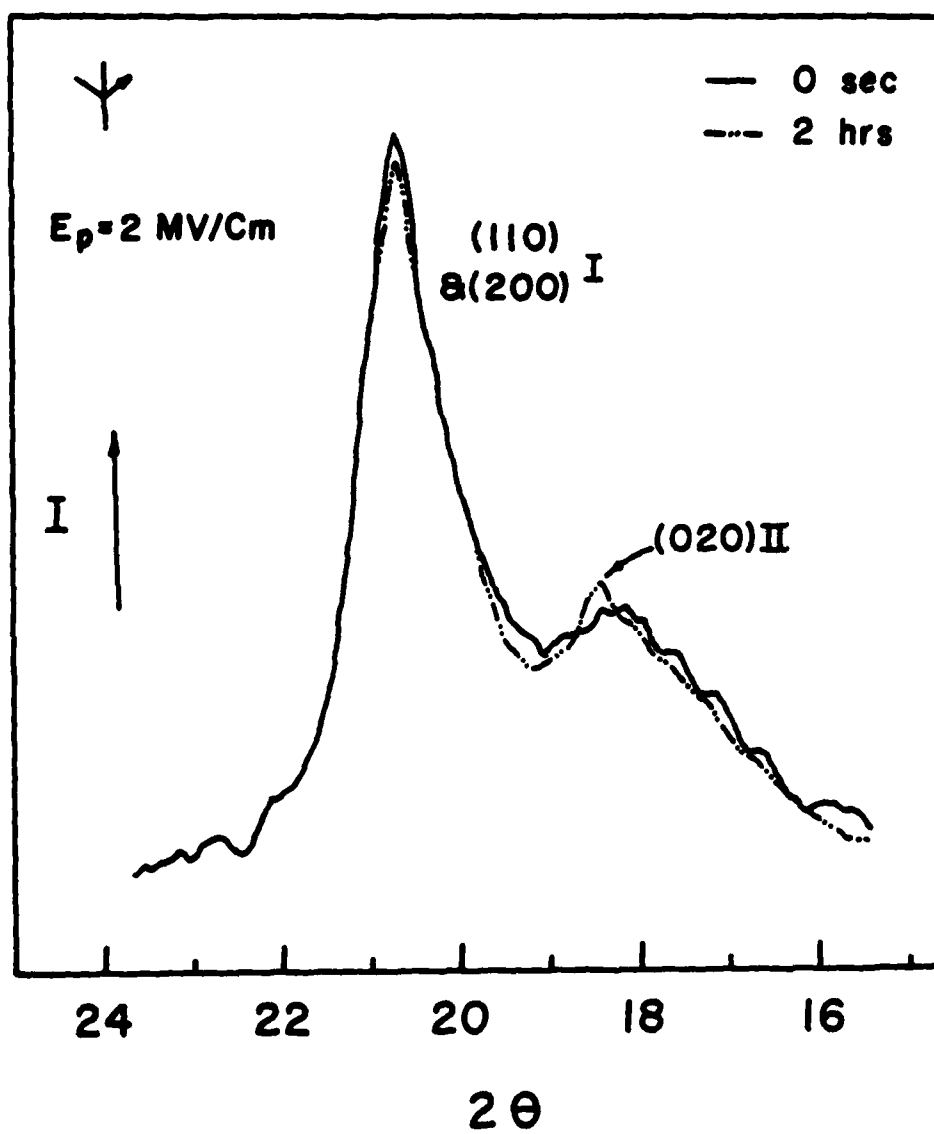
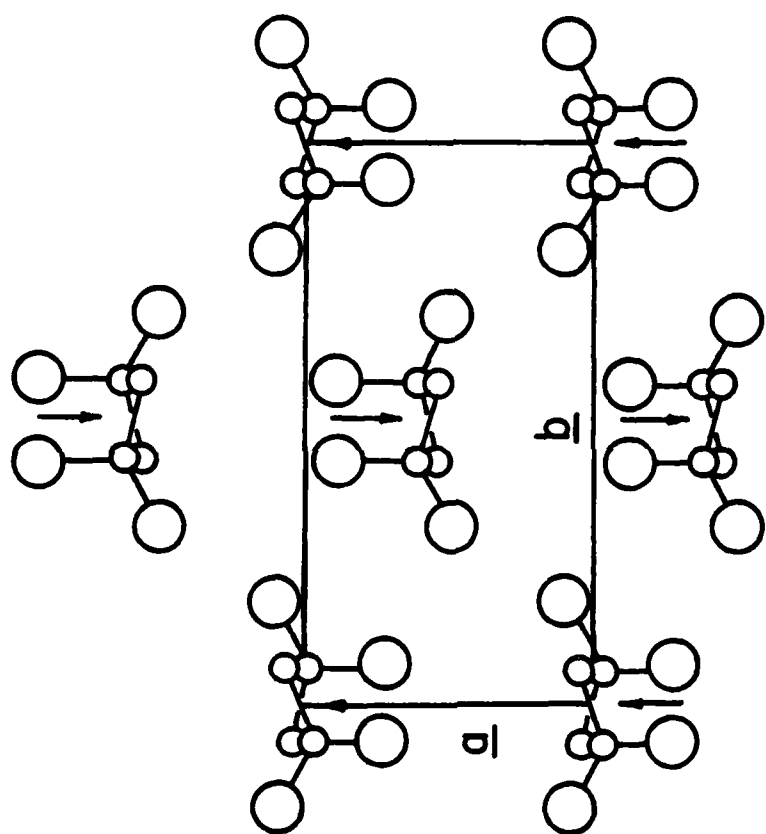


Fig 2









299

