

AD-A164 683

FIELD INDUCED DIPOLE REORIENTATION AND PIEZOELECTRICITY 1/1  
IN HEAVILY PLASTI.. (U) RUTGERS - THE STATE UNIV  
PISCATAWAY NJ DEPT OF MECHANICS AND H..

UNCLASSIFIED

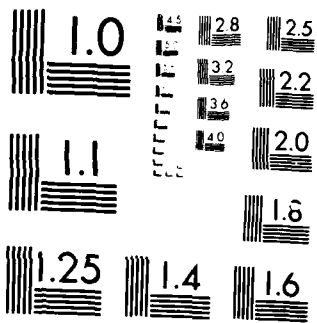
J I SCHEINBEIN ET AL. 86 JAN 86 TR-6

F/G 9/3

NL


FILMED

ETC.



MICROCOPY RESOLUTION TEST CHART  
NATIONAL BUREAU OF STANDARDS-1963-A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

21

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER Technical Report #6		2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Field Induced Dipole Reorientation and Piezoelectricity in Heavily Plasticized Nylon 11 Films		5. TYPE OF REPORT & PERIOD COVERED Technical	
7. AUTHOR(s) J.I. Scheinbeim, S.C. Mathur and B.A. Newman		6. PERFORMING ORG. REPORT NUMBER	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Dept. of Mechanics and Materials Science College of Engineering, Rutgers University Piscataway, New Jersey 08854		8. CONTRACT OR GRANT NUMBER(s) N-00014-80-C-0795	
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE January 6, 1986	
		13. NUMBER OF PAGES 26	
		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	

AD-A164 683

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.

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

DTIC ELECTED  
S FEB 19 1986 D

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  
Nylon 11, plasticizer, piezoelectric

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  
Nylon 11 films with very low initial crystallinity were made by dissolving the nylon 11 in 2-Ethyl 1,3 Hexanedioil at 150°C. Films were cast from the solution and excessive plasticizer was removed in a vacuum oven. Films were then melt-pressed and quenched to yield heavily plasticized nylon 11 films containing 30% by weight of the plasticizer. These films were poled under vacuum to allow the plasticizer to evaporate in the presence of an electric field. A high piezoelectric response ( $d_{31} = 7.1$  PC/N) was observed for the films subjected to the

FILE COPY

UNCLASSIFIED

---

maximum electric field ( $E_p = 350 \text{ KV/cm}$ ) while the sample contained a large fraction of plasticizer. Significant development of crystallinity was observed without apparent indication of orientation of the crystallites. These studies suggest that the observed piezoelectric response originates primarily from oriented hydrogen bonds in the amorphous regions of Nylon 11.

OFFICE OF NAVAL RESEARCH  
Contract N00014-80-C-0795  
Technical Report No. 6

FIELD INDUCED DIPOLE REORIENTATION AND PIEZOELECTRICITY IN  
HEAVILY PLASTICIZED NYLON 11 FILMS

by

J.I. Scheinbeim, S.C. Mathur and B.A. Newman  
Department of Mechanics and Materials Science  
College of Engineering  
Rutgers University  
Piscataway, New Jersey 08854

Prepared for Publication in

Journal of Polymer Science

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.

## INTRODUCTION

The general effects associated with plasticization of a polymer are a shift in the glass transition temperature to lower temperatures, reduction in the modulus, and an increase in the dielectric constant. Plasticizers are supposed to modify primarily the amorphous phase of a semicrystalline polymer. Most studies of the piezoelectric response of semicrystalline polymers have been concerned with the crystalline regions. For the case of Polyvinylidene fluoride ( $PVF_2$ ), it is well known that film polarization results from ferroelectric switching of polar crystallites [1, 2] and field induced crystal transitions from nonpolar to polar or polar to more polar structures [3, 4, 5, 6, 7]. However, several studies have indicated that the importance of the modification of the amorphous component on the resulting piezoelectric response cannot be neglected. Newman et. al. [8] have reported the effects of plasticization on the piezoelectric properties of unoriented (before poling)  $PVF_2$  films. Tricresyl Phosphate was used as the plasticizer and at about 3% plasticizer content by weight, the piezoelectric strain constant,  $d_{31}$ , was observed to have increased by 20%. The behavior of  $e_{31}$ , however, depended on whether the films were plasticized before poling or after poling. The values of  $e_{31}$  were observed to increase in the former case, while a decrease of about 20% was observed in the latter case. In a recent study by Sen et. al. [9], unoriented  $PVF_2$  phase II films (plasticized and unplasticized) and uniaxially oriented phase I films (obtained by stretching plasticized and unplasticized phase II films) were poled at different poling fields and X-ray studies were carried out to study the field induced crystal phase transitions. It was observed that field induced conversion to phase I took place at lower poling fields for plasticized,



	Codes
Dist	avail a.d/or Special
A-1	

initially unoriented, phase II films as compared to unplasticized films under identical poling conditions. The piezoelectric and pyroelectric response also increased with increasing plasticizer content.

In the case of nylons, Scheinbeim [10] observed that the piezoelectric strain constant,  $d_{31}$ , increased rapidly with increasing temperature as the Nylon 11 sample was heated through and above the glass transition temperature. The effect of water on the piezoelectric properties of Nylon 11 and Nylon 7 has been studied by Kim [11]. Water acts as a plasticizer for nylons and is expected to modify primarily the amorphous regions. It was observed that the value of  $d_{31}$  increased with an increase in the amount of absorbed water. The effect of plasticization (before poling) on the piezoelectric properties of unoriented and uniaxially oriented Nylon 11 films was studied using 2-Ethyl, 1-3 Hexanediol as the plasticizer [12, 13]. For both quenched and slow crystallized films, the value of  $d_{31}$  was observed to increase with increased amounts of plasticizer in the films. For the case of slow crystallized films, which are known to show very low piezoelectric response [14], the values of  $d_{31}$  increased rapidly upon poling of the plasticized and oriented films [15]. In recent studies [11] of the crystal structure of Nylon 11, it was suggested that the crystal form found in films slow cooled from the melt are probably nonpolar and that for films quenched from the melt, the quenched form [called the  $\delta'$  form] does not actually have long range three dimensional ordering but has an amorphous or quasi-amorphous nature. The response has been observed to increase with increasing content of the quenched phase (or the amorphous phase)[11]. These studies raise interesting questions about the origins of piezoelectricity in the odd nylons.

The presence of significant crystallinity in Nylon 11 actually reduces the piezoelectric response obtained after poling when compared to quenched, low crystallinity films. It may, therefore, be useful to study the piezoelectric properties of Nylon 11 films with very low initial crystallinity. For this purpose, it was decided to make Nylon 11 films with very high plasticizer content so that the initial crystallinity would be very low. In previous studies [12, 13], it was observed that it was not possible to obtain films with very high amounts of plasticizer without the use of elevated temperatures and longer lengths of time. In addition, if the quenched Nylon 11 films were immersed in plasticizer for more than 15 minutes at 75° C, then a crystal phase transformation or crystallization into the  $\alpha'$  form [12] started to occur. A different plasticization method was employed in the current set of experiments as described later. If we apply an electric field across these films and simultaneously let the plasticizer evaporate, then the crystallization process should be biased and we should expect preferential alignment of the dipoles in the field direction resulting in oriented crystalline growth. The dipoles in the amorphous regions should also be aligned in the field direction and as the plasticizer comes out and polymer-polymer hydrogen bonds form, their alignment should be frozen-in. If the predominant contribution to the piezoelectric response, is from the amorphous fraction, then we should expect the maximum response from the samples for which the electric field is applied while the plasticizer content is very large and for which little or no oriented crystal growth occurs. On the other hand, if the crystalline regions provide the predominant contribution, then we should expect a significant amount of oriented crystal growth.



## EXPERIMENTAL

The plasticizer used in this study was 2-Ethyl 1,3 Hexanediol. Nylon 11 was dissolved in the plasticizer at 150° C and then films were cast from the solution (containing ~20% by weight of nylon 11). As soon as the temperature began to decrease, the solution became very viscous. At room temperature, the evaporation rate of plasticizer was very slow. In order to remove excessive plasticizer, the cast films were placed in a vacuum oven ( $\sim 10^{-3}$  torr) and the plasticizer was allowed to evaporate at 50°C. As the rate of evaporation of the plasticizer was faster from the top surface than from the bottom surface, many cracks developed in the films. In order to obtain films with sufficient mechanical and electrical strength so that samples could be handled and poled without extreme difficulties, the films were melted between aluminum foil at 200° C, pressed at 1000 psi and then quenched into ice water. Final plasticizer content was estimated to be ~30% by weight in these films. Wide angle diffractometer scans were taken for these films and the crystallinity was determined to be 15%.

For poling purposes, silver paint was used to form electrodes on the films. Poling was done under high vacuum ( $\sim 10^{-6}$  torr) and it was observed that the plasticizer began to come out at room temperature ( $\sim 22^\circ$  C) under this vacuum. Figure 1 shows a schematic representation of the poling set-up. For measurements of the piezoelectric constants, modulus and dielectric constant, the hard silver paint was removed and a soft silver paste was used to serve as electrodes. Preliminary studies were made to obtain optimum poling parameters: maximum poling field, poling temperature and poling time. As far as poling time is concerned, two different time periods were defined. Initially, some time elapsed before the final (maximum) poling field is

reached as the field is ramped up at a fixed rate using a programmed voltage ramper. We denote the time to reach the maximum poling field as  $t_E$ . The time for which the sample is held at the maximum poling field is denoted as  $t_p$  and the maximum poling field as  $E_p$ . The schematic diagram shown in figure 2 indicates these different parameters. Three different kinds of experiments were performed:

(a) In the first experiment, the poling field was chosen as 300 KV/cm. From weight change measurements of the samples, it was observed that the plasticizer came out rapidly during the first 30 minutes and, therefore,  $t_E$  was chosen as 30 minutes. The samples were poled at  $\sim 22^\circ$  C for different lengths of time,  $t_p$ . The measurements of  $d_{31}$ ,  $e_{31}$ , modulus and dielectric constant were made as a function of  $t_p$ .

(b) In the second experiment,  $t_E$  was fixed at 30 minutes and  $t_p$  was chosen as 30 minutes (obtained from the results of the previous experiment) and the samples were poled at different poling fields. All these measurements were performed as a function of poling field.

(c) From the results of the previous two experiments, it was observed that a poling field of 350 KV/cm was the maximum that could be used without the occurrence of excessive dielectric breakdown. A poling time,  $t_p$ , of 30 minutes produced a saturation in the response. In this experiment, it was decided to ramp up to the poling field faster, so that the maximum poling field was reached while the sample still contained large amounts of plasticizer and the crystallinity was also low. The schematic representation of this experiment is shown in figure 3. The fastest rate was limited by the dielectric strength of the sample which is lower for samples containing larger amounts of plasticizer. Measurements of  $d_{31}$ ,  $e_{31}$ , modulus, and dielectric constant were performed as a function of ramping time ( $t_E$ ).

## RESULTS AND DISCUSSIONS

### A. Development of crystallinity

Figure 4 represents the variation of plasticizer content with total poling time and the simultaneous increase in crystallinity. The solid line for the variation of plasticizer content represents the decrease in the bulk plasticizer content. However, the plasticizer is expected to be primarily present in the amorphous regions. The dashed line shows the variation of the plasticizer content in the amorphous regions, obtained by calculation after providing necessary corrections for the increase in crystallinity. Plasticizer comes out rapidly during the first 30 minutes in the high vacuum used for poling and then levels off at ~11% plasticizer content by weight. The crystallinity also increases during the first 30 minutes and then the curve flattens as the evaporation of plasticizer decreases. This might be an indication of the glass transition phenomenon. As the plasticizer level drops to ~11%, the glass transition temperature might have reached the ambient temperature (~22° C) and the evaporation of plasticizer decreases and further crystallization of the film is inhibited.

### B. Poling time, $t_p$ , dependence

Figures 5 and 6 show the variations of  $d_{31}$  and  $e_{31}$  respectively, with different poling times,  $t_p$ . It should be noted that the poling field was slowly ramped up over 30 minutes ( $t_E$ ) and that the poling times are over and above this time period of 30 minutes. Both  $d_{31}$  and  $e_{31}$  increased with increasing poling time and the values tended to saturate at  $t_p = 30$  minutes. At this point, the value of  $d_{31}$  was 2.0 PC/N and the corresponding value for  $e_{31}$  was 0.7 mC/m<sup>2</sup>. The values for modulus and dielectric constant remain essentially unchanged for these samples, the modulus being  $\sim 0.3 \times 10^{10}$  dynes/cm<sup>2</sup> and the value of dielectric constant being 16.0. All the samples

contained 11% by weight of the plasticizer after poling. The rapid decrease in plasticizer content in the poling set-up occurs during the first 30 minutes. From these preliminary experiments, it was decided to use 30 minutes as the poling time for the next set of experiments.

#### C. Poling field dependence

The purpose of this set of experiments was to determine the maximum poling field that could be used with these films without producing dielectric breakdown. The poling field ramping time,  $t_E$ , was taken as 30 minutes and the poling time,  $t_p$ , was also 30 minutes. Figures 7 and 8 show the variation of  $d_{31}$  and  $e_{31}$  with poling field. The poling was done at room temperature. Both  $d_{31}$  and  $e_{31}$  increased rapidly with poling field with no indication of saturation up to the fields used in this study. The maximum poling field that could be used without dielectric breakdown was found to be 350 KV/cm.

#### D. Poling field ramping time, $t_E$ , dependence

For both of the above studies the field was ramped up slowly over the 30 minutes time during which, the plasticizer rapidly came out from the film under vacuum. Our next objective was to see if we could ramp up the field faster, so that the maximum field would be reached while the samples still contained large amounts of plasticizer. Since it has been suggested that the major piezoelectric response in Nylon 11 originates from the amorphous fractions containing oriented hydrogen bonded amide groups [11], we should expect an enhancement in the response if the poling field is applied while the mobility of the amorphous fractions is large i.e., larger amounts of plasticizer are present in the sample. Using a programmed voltage ramper, different rates of ramping were chosen so that the poling field of 350 KV/cm would be reached in different lengths of time. The schematic representation of this experiment is shown in figure 3. The poling time,  $t_p$ , was kept

constant at 30 minutes once the maximum poling field was reached. The results of this study for  $d_{31}$  and  $e_{31}$  are shown in figures 9 and 10 respectively. The values for both  $d_{31}$  and  $e_{31}$  increase as ramping time (time to reach  $E_p$ ) is lowered. The lowest  $t_E$  that could be used was 7 minutes. Excessive dielectric breakdown occurred once the ramping time was near 10 minutes. The limitation of ramping time comes from the fact that with the presence of larger amounts of plasticizer, the dielectric strength of the films is lower. The value of  $d_{31}$  rises from 4.0 PC/N at  $t_E = 30$  minutes to 7.1 PC/N for a  $t_E$  of 7 minutes. The corresponding increase in  $e_{31}$  is from 1.2 mC/m<sup>2</sup> to 2.2 mC/m<sup>2</sup>.

These results can be understood in general terms by the following admittedly simplistic model. The plasticizer is expected to form hydrogen bonds with the amide groups of the molecular chains of the heavily plasticized nylon 11 in the amorphous regions, and may prevent or limit formation of inter or intramolecular hydrogen bonding of the polymer chains. Under the action of the electric field, the amide groups which are hydrogen bonded with the plasticizer molecules may orient with the plasticizer molecules so that their dipole direction becomes aligned in the field direction. Under vacuum, the plasticizer diffuses out and the oriented amide groups may now form either intermolecular or intramolecular hydrogen bonds. When the electric field is removed, the preferred direction of alignment of dipoles persists since randomization of dipoles can occur only when enough thermal energy is available (by raising the temperature) to break the hydrogen bonds. Unbonded plasticizer molecules, and plasticizer molecules which are hydrogen bonded with the amide groups to form bridges between chains may also play a role in this process. In any event, the stability of hydrogen

bonds which involve plasticizer molecules is expected to be less than that of the intermolecular or intramolecular hydrogen bonds.

X-ray studies were carried out to observe the development of crystallinity as the plasticizer was removed in the presence of the poling field. Figure 11 shows wide angle x-ray diffraction scans, in reflection mode, for these films before and after poling. The estimated crystallinity increases from  $\sim 15.2\%$  to  $\sim 44\%$  for the samples poled with a ramping time of 7 minutes. Figure 12 shows the schematic representation of the flat-film x-ray pictures in an edge reflection mode (x-ray beam parallel to the plane of the film). A comparison of the flat-film x-ray diffraction patterns of an unpoled film (with the same history as the poled sample but with no poling field applied) with a poled sample indicates that there is no significant difference in diffraction pattern upon poling.

The most interesting thing to note here is that there is no indication of any orientation of the crystallites. Although we do not see any orientation effects in the crystallites, we do see an enormous increase in the piezoelectric response. This reinforces the possibility that the origin of the piezoelectric activity in Nylon 11 does not lie in the crystalline regions, or may possibly indicate that the x-ray diffraction from Nylon 11 is insensitive to the amide group (hydrogen bond) orientation. In the presence of an electric field, we expected dipole alignment in the field direction to occur in the crystalline regions also. The absence of any arcing in the debye rings could be due to the possibility that the major reflections are coming from a hydrocarbon sub-cell structure as reported for  $\alpha'$  form nylon 11 and nylon 7 by Kim [11]. This will be investigated in future work.

## CONCLUSIONS

In this study, we have developed a unique method of making plasticized Nylon 11 films with very high piezoelectric response. The maximum observed values for  $d_{31}$  are more than double the values previously observed for un-plasticized films [14]. Earlier studies [11] have shown that the piezoelectric response of Nylon 11 increased with increasing amounts of amorphous (or  $\delta'$ ) phase. The results from our poling field-ramping time studies indicate that the origin of the piezoelectric response for nylon 11 most probably lies with the amorphous fraction rather than the crystalline fraction. The response depends upon the application of an electric field while the plasticizer content is high and the mobility of the amorphous material is also high. The presence of an electric field does not seem to influence the development of crystallinity and the crystal structure. Absence of any apparent indication of orientation of the crystallites could be explained if the principal reflections arise from a hydrocarbon subcell structure rather than from the Nylon 11 unit-cell. The maximum piezoelectric response appears to be limited only by the dielectric strength of the plasticized sample.

## ACKNOWLEDGMENT

This work was supported in part by the Office of Naval Research.

## REFERENCES

1. P. Buchman, *Ferroelectrics*, 5, pp. 39, 1973.
2. J.I. Scheinbeim, C.H. Yoon, K.D. Pae and B.A. Newman, *J. Appl. Phys.*, 51, p. 5156, 1980.
3. G.T. Davis, J.E. McKinnery, M.G. Broadhurst and S.C. Roth, *J. Appl. Phys.* 49, p. 4998, 1978.
4. B.A. Newman, C.H. Yoon, K.D. Pae and J.I. Scheinbeim, *J. Appl. Phys.*, 51, p. 5161, 1979.
5. P.D. Southgate, *Appl. Phys. Lett.*, 28, p. 250, 1976.
6. D.K. Dasgupta, K. Doughty, *Appl. Phys. Lett.*, 31, p. 585, 1977.
7. D.K. Dasgupta, K. Doughty, *J. Appl. Phys.*, 49, p. 4601, 1978.
8. B.A. Newman, J.I. Scheinbeim and A. Sen, *Ferroelectrics*, 57, p. 229, 1984.
9. A. Sen, J.I. Scheinbeim, and B.A. Newman, *J. Appl. Phys.*, 59, p. 2433, 1984.
10. J.I. Scheinbeim, *J. Appl. Phys.*, 52, p. 5939, 1981.
11. K.G. Kim. Ph.D. Thesis, Mechanics and Materials Science, Rutgers University, 1985.
12. S.C. Mathur, J.I. Scheinbeim and B.A. Newman, manuscript in preparation.
13. S.C. Mathur, J.I. Scheinbeim and B.A. Newman, manuscript in preparation.
14. B.A. Newman, P. Chen, K.D. Pae and J.I. Scheinbeim, *J. Appl. Phys.*, 51, p. 5161-5164, 1980.
15. S.C. Mathur, J.I. Scheinbeim and B.A. Newman, *J. Appl. Phys.*, 56, p. 2419-2425, 1984.



## FIGURE CAPTIONS

1. Schematic representation of the Poling set-up
2. Schematic representation of the various parameters in the poling process
3. Schematic representation of variation in the poling field ramping rates
4. Variation of plasticizer content and increase in crystallinity with time
5. Variation of piezoelectric strain constant,  $d_{31}$ , with poling time,  $t_p$
6. Variation of piezoelectric stress constant,  $e_{31}$ , with poling time,  $t_p$
7. Poling field dependence of  $d_{31}$
8. Poling field dependence of  $e_{31}$
9. Variation of  $d_{31}$  with poling field ramping time,  $t_E$
10. Variation of  $e_{31}$  with poling field ramping time,  $t_E$
11. X-ray diffraction scans, in reflection mode, before and after poling for different poling field ramping times
12. Schematic representation of the x-ray picture in edge reflection mode for poled and unpoled films

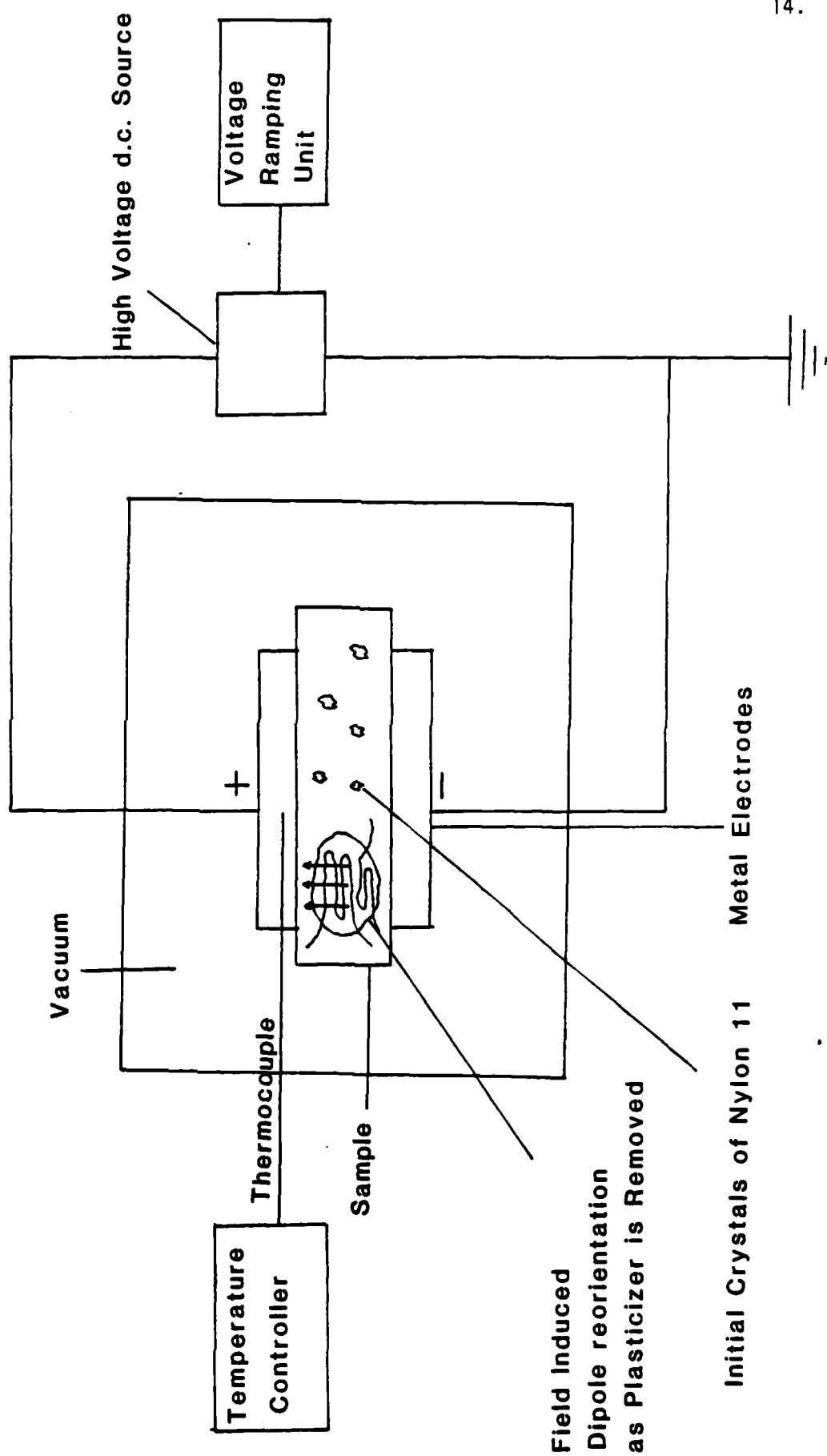


FIGURE 1

Field Induced  
Dipole reorientation  
as Plasticizer is Removed

Initial Crystals of Nylon 11      Metal Electrodes

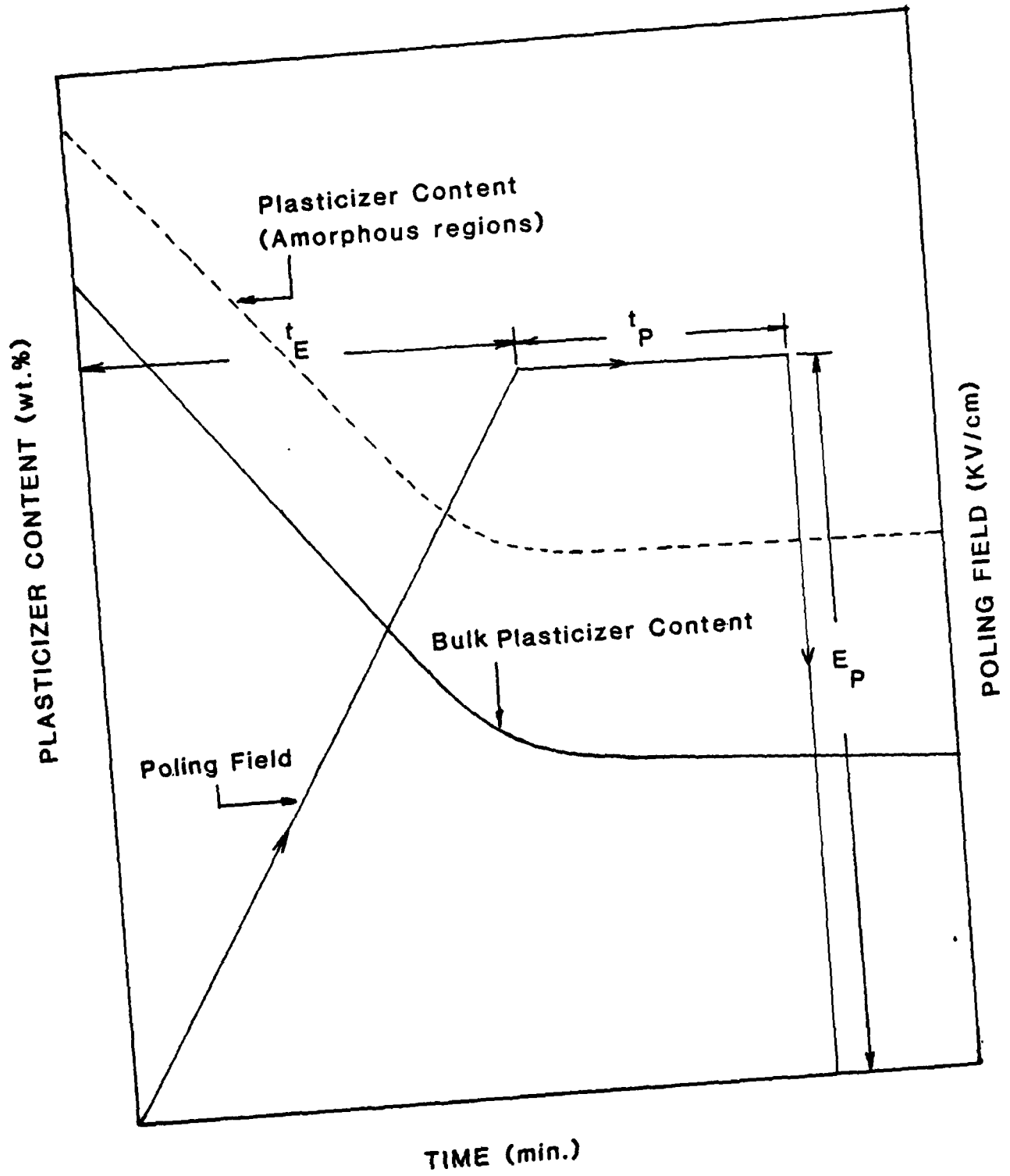


FIGURE 2

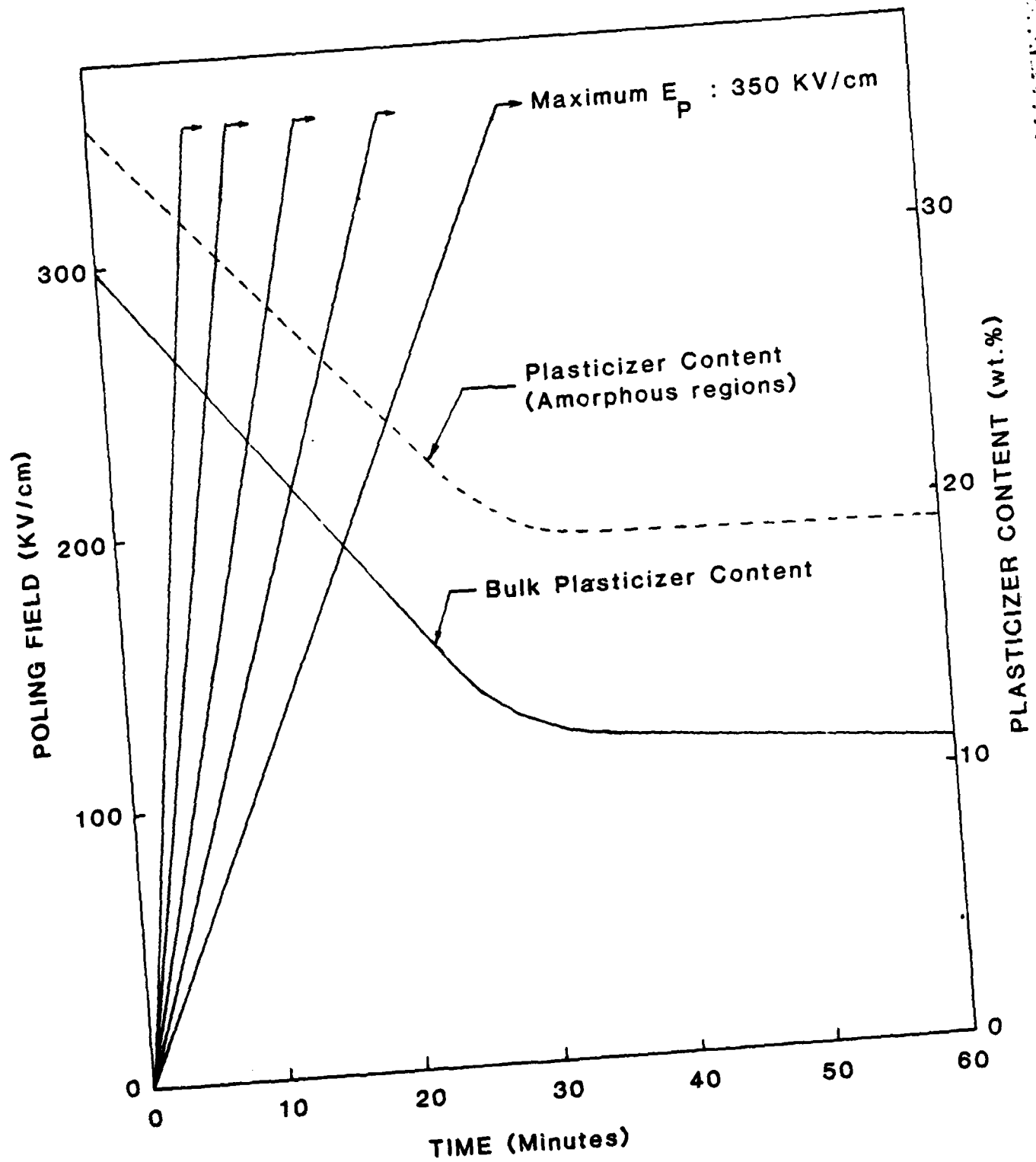


FIGURE 3

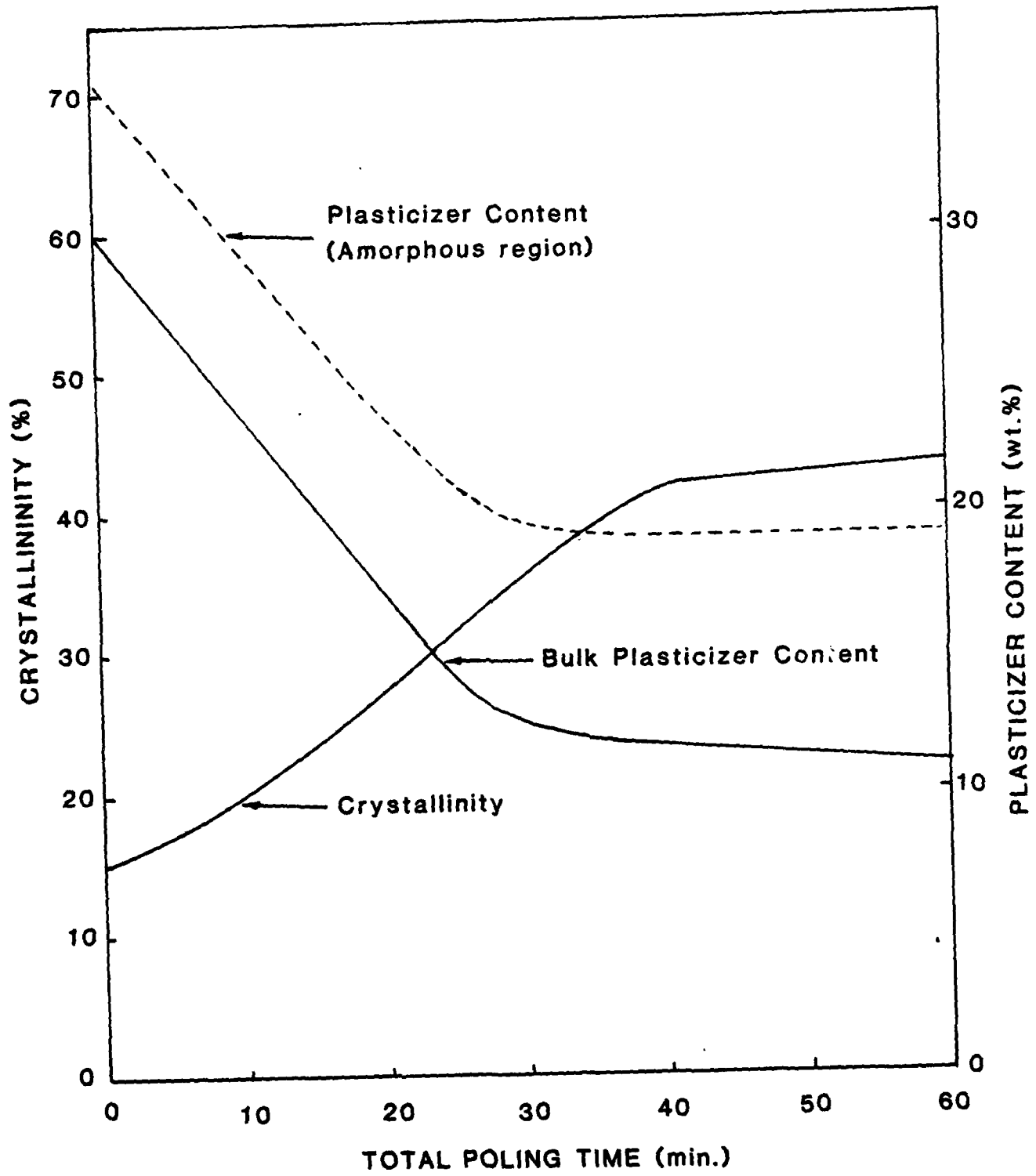


FIGURE 4

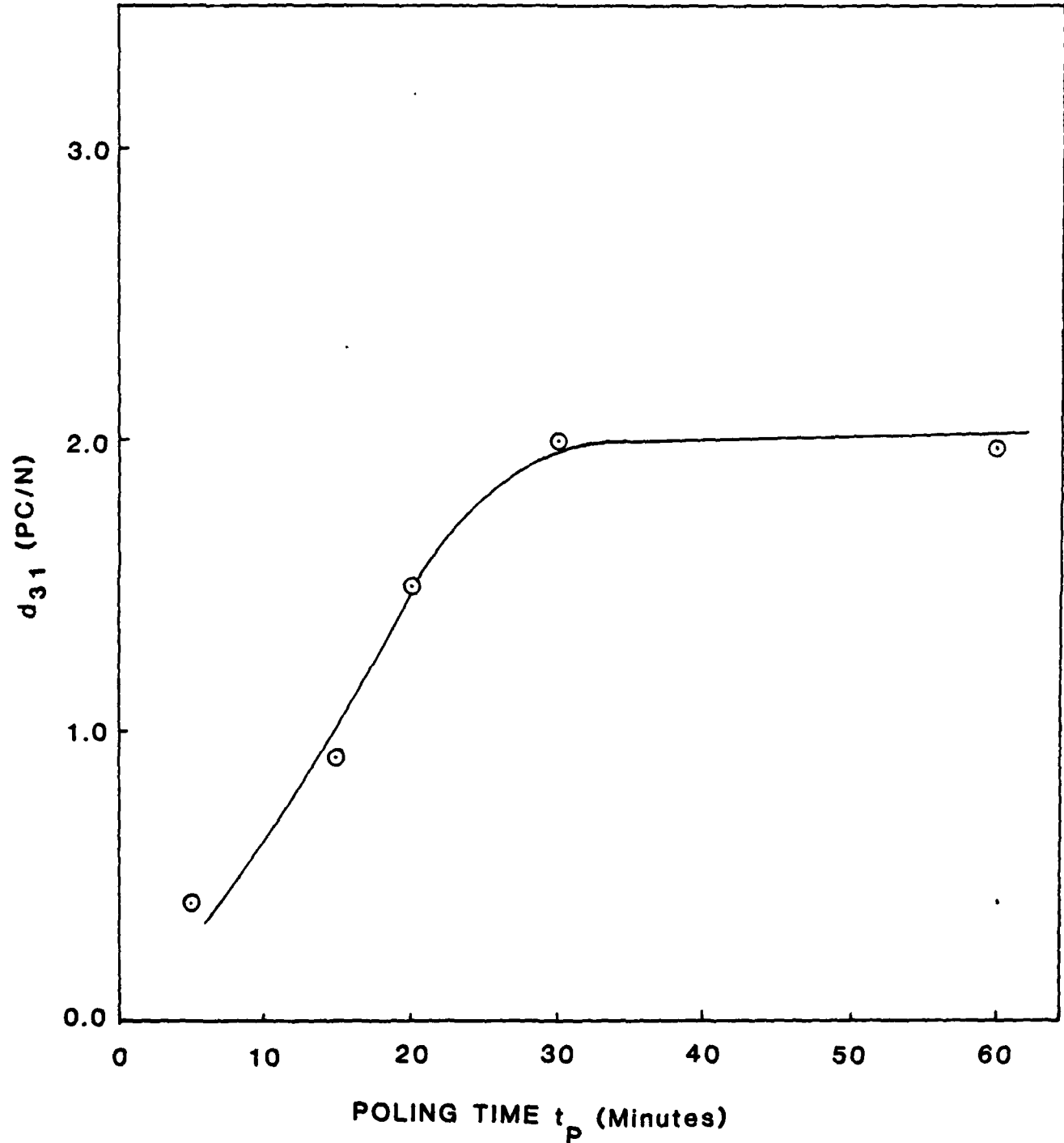


FIGURE 5

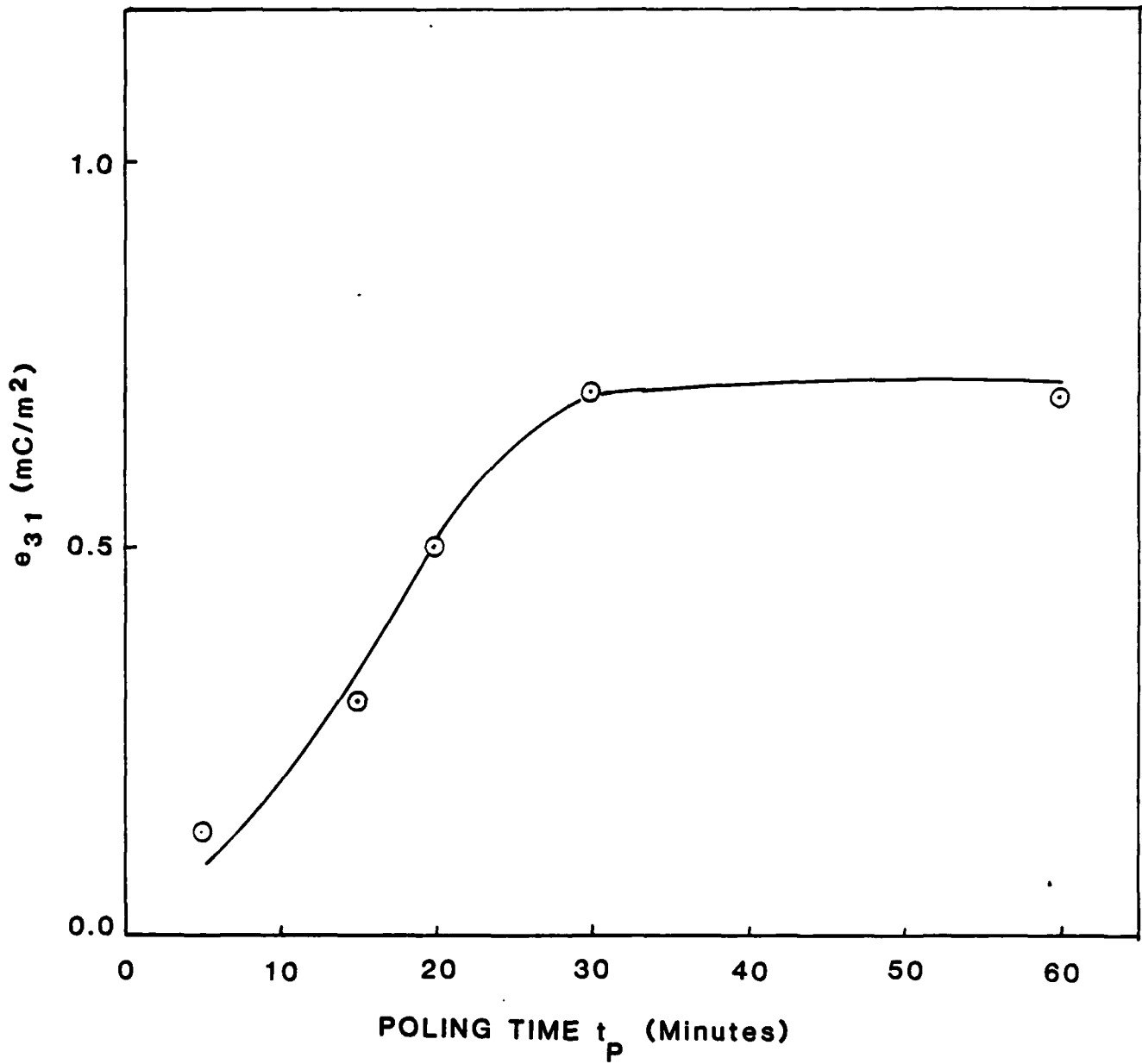


FIGURE 6

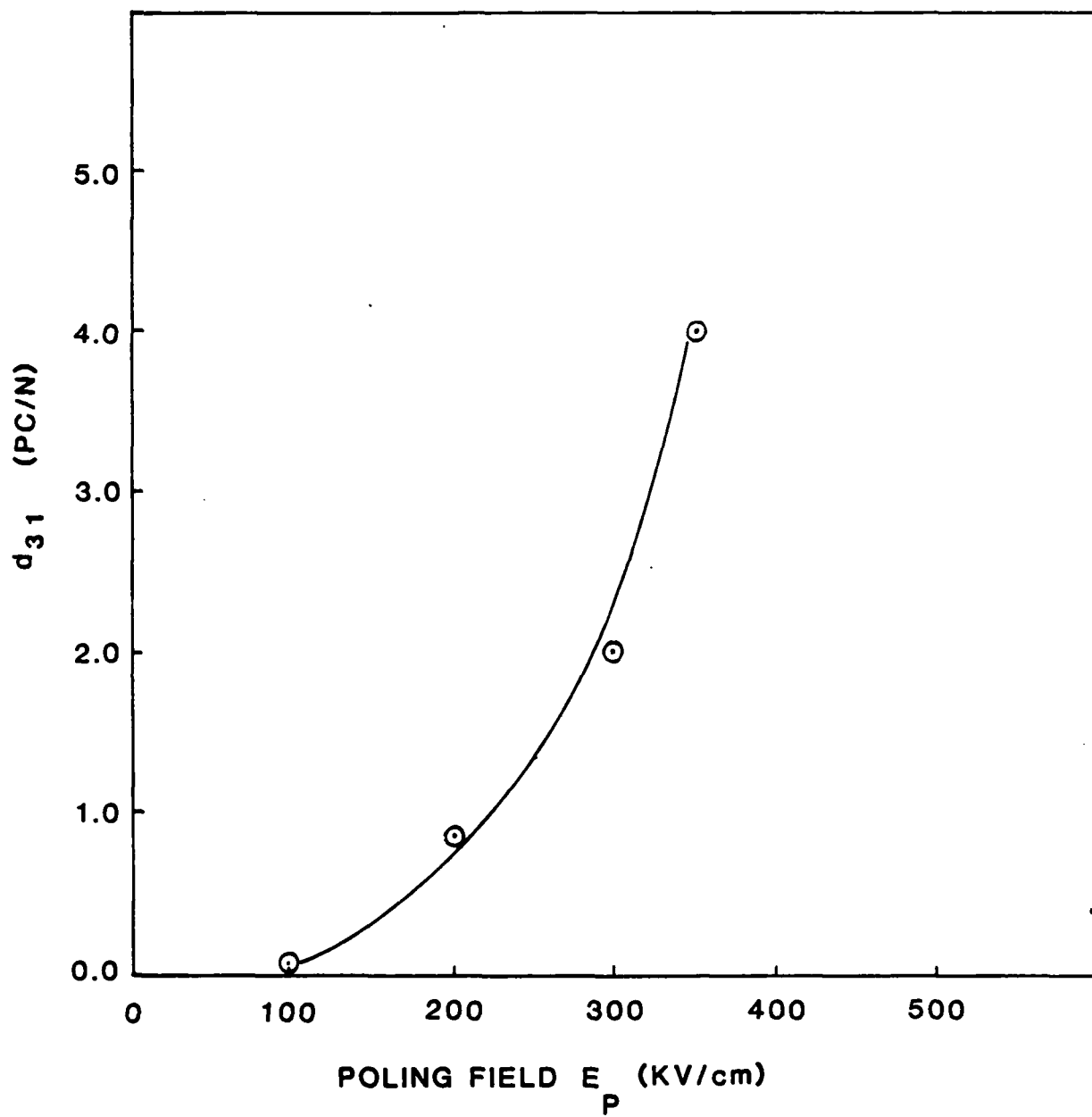


FIGURE 7



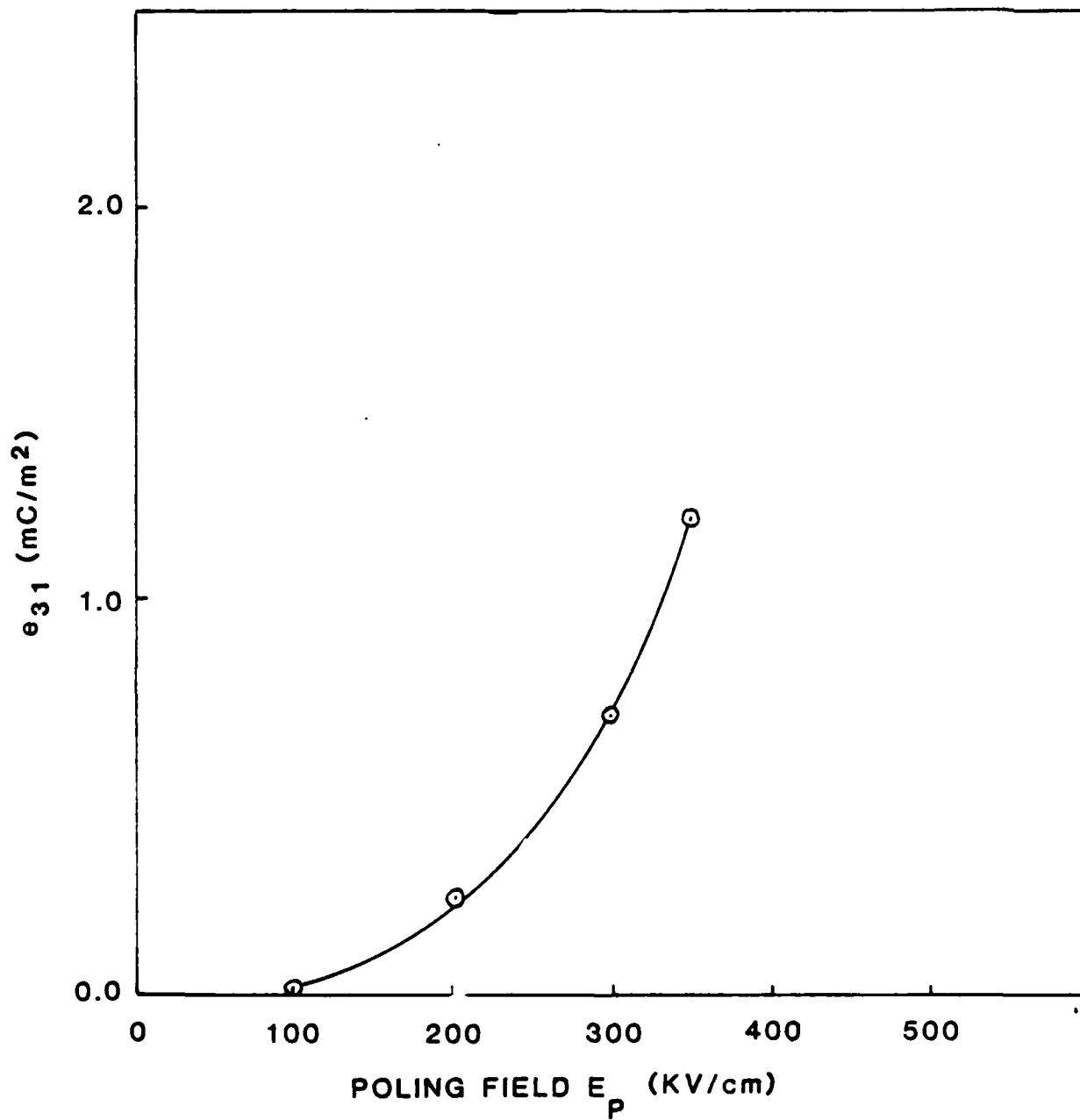


FIGURE 8

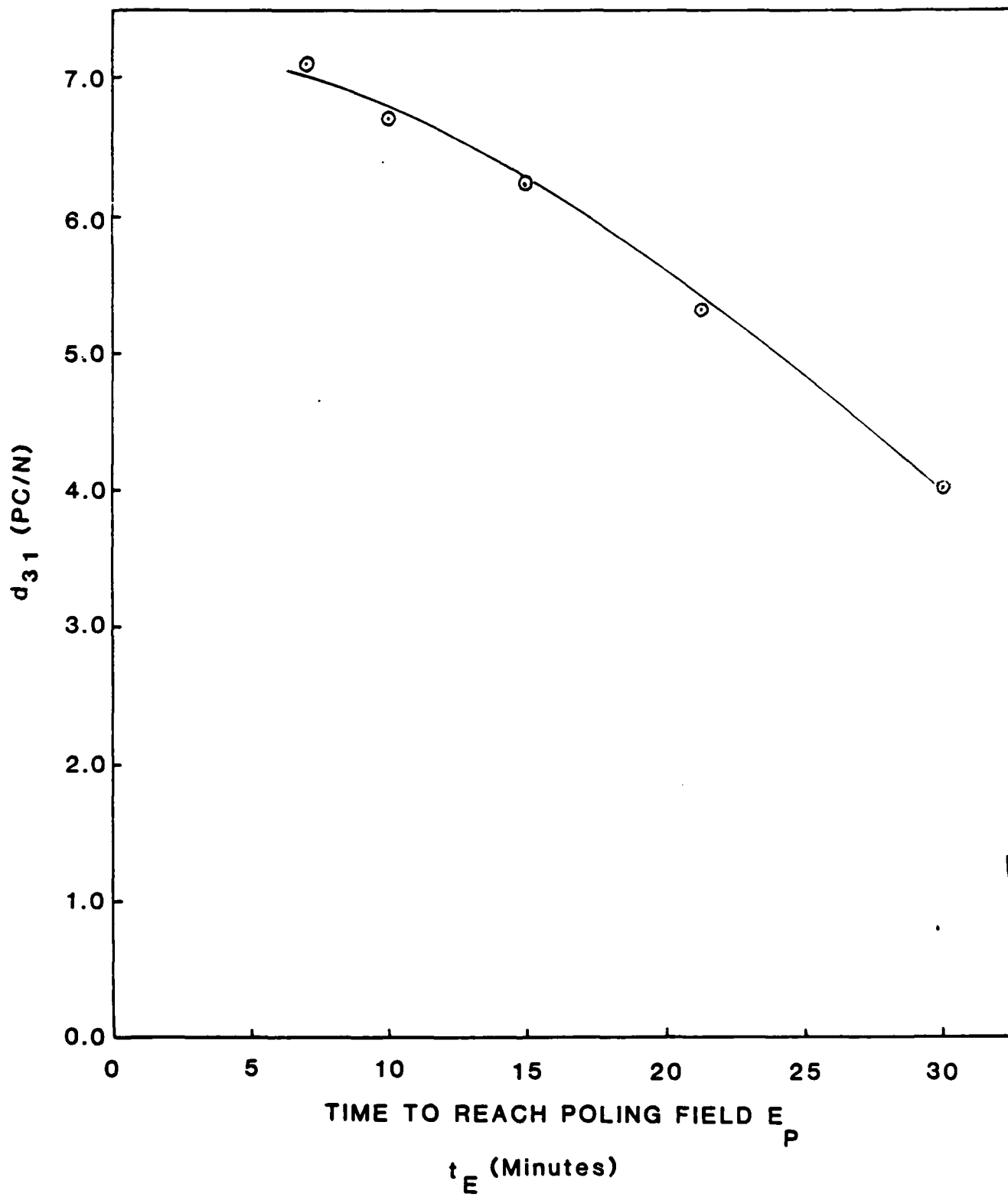


FIGURE 9

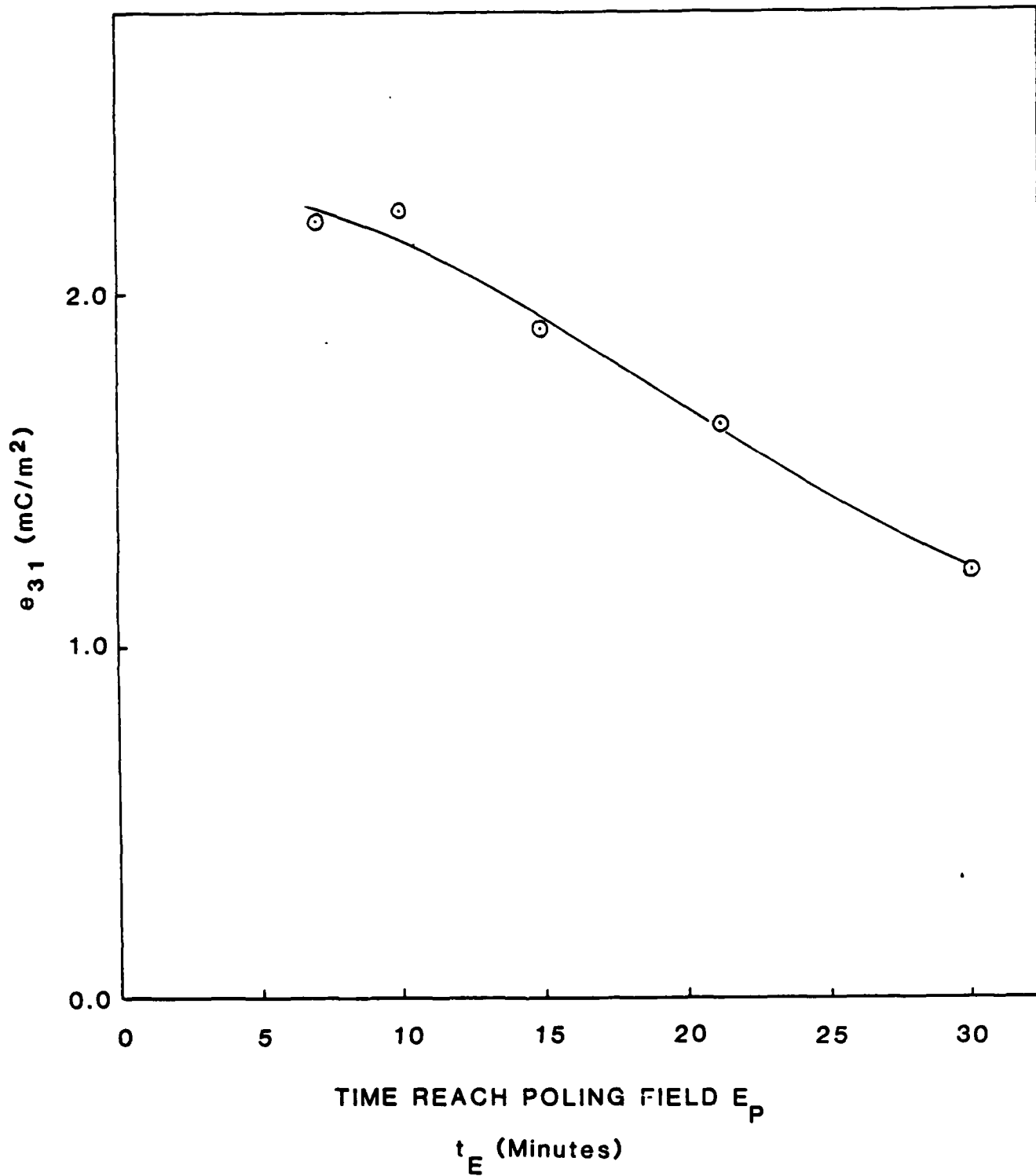


FIGURE 10

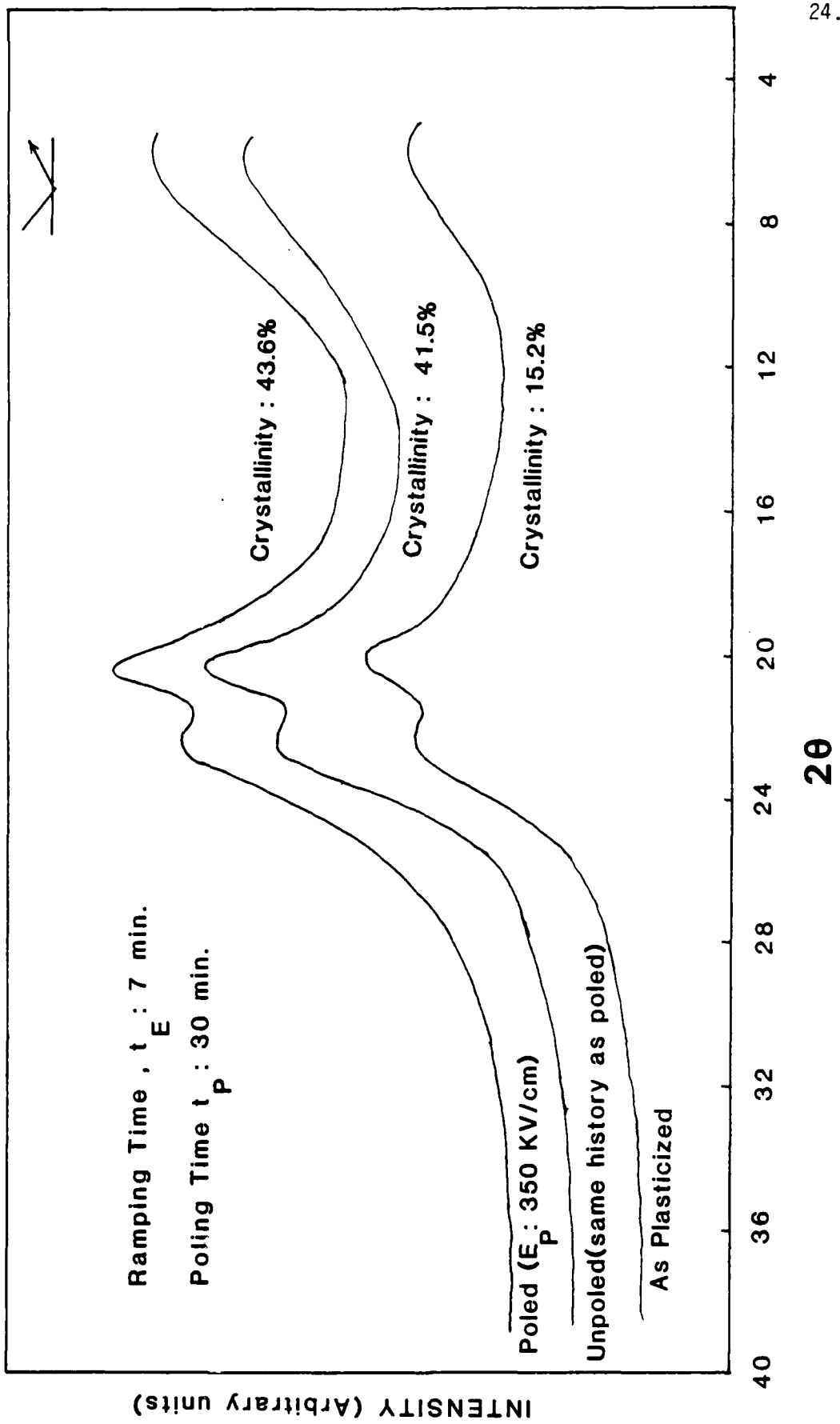
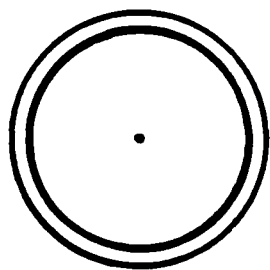
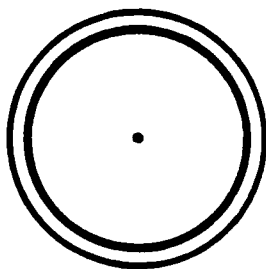


FIGURE 11

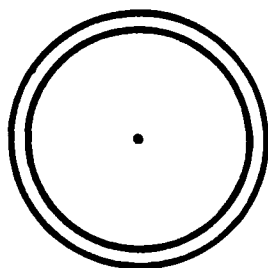
Schematic representation of X-ray diffraction patterns  
(X-ray beam parallel to the plane of the film)



As plasticized



Unpoled (same history as poled)



Poled  
 $E_P$  : 350 KV/cm  
 $t$  : 7 min.  
 $E$

FIGURE 12

**END**

**FILMED**

4-86

**DTIC**