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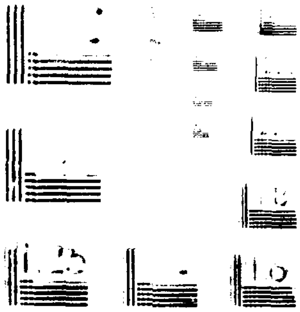
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At the present time, only poled, drawn poly(vinylidene fluoride)(PVF_2) films give evidence of sufficiently high piezoelectric response to be useful in device applications, and for this reason the great majority of research has centered around this polymer. As in the case of PVF_2, many of the odd nylons crystallize in a polar space group with a large net dipole moment in the unit cell. On the basis of the understanding now reached of the properties of poled PVF_2 films it would appear that the odd nylons have the potential to

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make films with high piezoelectric activity. Piezoelectricity and pyroelectricity in nylon 11 films have been studied previously and piezoelectric strain coefficients found were higher than most polymers but still two orders of magnitude less than the corresponding activity found in poled oriented PVF_2 ($d_{31} \sim 20$pC/N). Studies carried out in this laboratory have shown that by appropriate variation of poling conditions and sample microstructure quite large piezoelectric constans can be obtained for nylon 11 films ($d_{31} \sim 3$pC/N). The dependence of the piezoelectric strain constant d_{31} on poling tempeature, poling field and crystal structure will be discussed.

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PIEZOELECTRICITY IN NYLON 11

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Abstract

At the present time, only poled, drawn poly(vinylidene fluoride)(PVF_2) films give evidence of sufficiently high piezoelectric response to be useful in device applications, and for this reason the great majority of research has centered around this polymer. As in the case of PVF_2, many of the odd nylons crystallize in a polar space group with a large net dipole moment in the unit cell. On the basis of the understanding now reached of the properties of poled PVF_2 films it would appear that the odd nylons have the potential to make films with high piezoelectric activity. Piezoelectricity and pyroelectricity in nylon 11 films have been studied previously and piezoelectric strain coefficients found were higher than most polymers but still two orders of magnitude less than the corresponding activity found in poled oriented PVF_2 (d_{31}~20pC/N). Studies carried out in this laboratory have shown that by appropriate variation of poling conditions and sample microstructure quite large piezoelectric constants can be obtained for nylon 11 films (d_{31}~3pC/N). The dependence of the piezoelectric strain constant d_{31} on poling temperature, poling field and crystal structure will be discussed.

Introduction

Since the first reported studies of high piezoelectric activity in poled polymer films(1-3), the potential applications of these films have excited considerable attention. At the present time only poly(vinylidene fluoride) (PVF_2) gives evidence of sufficiently good electrical properties to be useful in device applications and for this reason the great majority of research has been concerned with this polymer.

Although much work remains to be done with PVF_2 in order to provide a complete understanding of the relationship between piezoelectric properties, poling conditions, crystal structure morphology and molecular orientation, an understanding of the phenomena in general terms, for PVF_2, has been reached. It now appears clear that piezoelectric and pyroelectric activity simply results from the aggregate properties of polar crystallites with preferred dipole orientation in an amorphous matrix. If the initial crystal structure of the unpoled film contains phase I (a polar phase) and phase II (a non-polar phase) the piezoelectric coefficients d_{31} and e_{31} have been found to be proportional to the mass fraction of phase I(4), after poling at low fields. If the initial crystal structure of the unpoled film is phase II (a non-polar phase), field-induced crystal structure transitions to other polar phases (phase I, phase III or a polar phase with the same unit cell dimensions as phase II which we will term phase IV) occur at high poling fields and give rise to a corresponding piezoelectric activity, depending on the field strength and orientation of the crystallites with respect to the field direction(5,6,7,8). A theoretical model developed by M. G. Broadhurst(9) and others based on oriented polar crystallites has been used to calculate piezoelectric coefficients for oriented films and gives values which are in rough agreement with experiment.

The all-trans conformations of the odd-nylon molecules such as nylon 11 give rise to a large dipole moment perpendicular to the chain, since the amide group has a large dipole moment (about 3.7D) and the all-trans conformation requires that all the molecular dipole moments are aligned in the same direction. Nylon 11 and nylon 7 can also crystallize with a large dipole moment in the unit cell of the crystalline phase. On the basis of the understanding now reached of the properties of PVF_2 films, it would appear that the odd nylons should also have the potential to make good piezoelectric films. The dipole density in crystallites of nylon 11 has been calculated to be $1.5D/100\mathring{A}^3$, using the structure reported by B. A. Newman, T. P. Sham and K. D. Pae(10).

Piezoelectricity and pyroelectricity in nylon 11 films have been studied by Kawai and Heiji(11,12) and also by Litt, Hsu and Basu(13). The piezoelectric strain coefficients reported were surprisingly low ($\sim 5.0\times10^{-9}$ cgsesu by Litt et al. and $\sim 10.0\times10^{-9}$ by Kawai and Heiji). These values are higher than most polymers but still two orders of magnitude less than the corresponding activity found in oriented PVF_2 films. Experience with PVF_2 has shown that the final piezoelectric activity is quite sensitive to poling conditions, and we decided that a more systematic study of the piezoelectric properties of poled nylon 11 films should be made.

A crystal phase transition in nylon 11 from the triclinic α-phase to a pseudo-hexagonal γ-phase at 95°C has previously been reported(10) and in view of the importance of crystal structure to piezoelectric properties found for PVF_2(7) we decided to investigate the importance of this feature in addition to poling temperature, poling time, and poling field.

Experimental

1. Film characterization.

Nylon 11 films 3 mil. thick were obtained from Rilsan Corporation. The samples were studied using a Perkin Elmer 1B Differential Scanning Calorimeter and a Philips x-ray diffractometer. The melting temperature was found to depend on the crystallization rate. Samples that were rapidly crystallized gave rise to an endothermic peak at 189°C and were observed to be γ-phase at room temperature. Samples that were slowly crystallized gave rise to an endothermic peak at 182°C and were observed to be α-phase at room temperature. Only unoriented films were used.

Two types of film were studied:

(a) films with the γ-structure stable at room temperature which corresponded to the rapidly crystallized films

(b) a film as described in (a) but subsequently annealed at 120°C for four hours and then slowly cooled to room temperature, where it was found to have recrystallized into the α-structure.

2. Poling methods and measurement of piezoelectric constant.

Previously(7), it was shown that high poling fields without breakdown could be achieved using a thick silver paste for electrodes during poling.

Voltages of up to 3.75 kV were taken from a high voltage power supply to produce fields of up to 500 kV/cm. The films were not dried and at temperatures of over 90°C the conductivity increased very rapidly leading to film breakdown, except at the very lowest fields. All the films were poled in vacuum for 30 minutes except for those used for a time dependence study. After poling, the films were cooled slowly to room temperature under field.

Measurements of the piezoelectric strain constant d_{31} and the piezoelectric stress constant e_{31} at 3Hz were made using a Toyo Seiki Piezotron.

Results and Discussion

Fig. 1(a) and (b) shows the results obtained for the rapidly crystallized films with the γ-phase structure stable at room temperature. The films were poled at three different fields 150 kV/cm, 330 kV/cm, and 550 kV/cm at various temperatures. Both the piezoelectric strain constant d_{31} and stress constant e_{31} are shown. It should be noticed that at the highest fields and temperatures, quite high values of d_{31} and e_{31} were obtained. The highest value for d_{31} = 3.2 pC/N compares with a value for unoriented PVF_2 phase I film of about ~7 pC/N$^{(4)}$. Since we estimated the dipole density for nylon 11 as 1.5D/100Å^3 compared with 2.9D 100Å^3 for PVF_2 (phase I), the values we obtained for d_{31} seem quite reasonable (although much higher than observed previously).

The piezoelectric activity depended on both poling temperature and poling field. Very little activity was found unless the poling temperature was greater than a critical value which appeared to be somewhat field dependent. At 500 kV/cm both d_{31} and e_{31} increased sharply when the poling temperature exceeded ~45°C. At lower fields, the increase in d_{31} and e_{31} with poling temperature was less marked. Very low values for d_{31} (less than 0.1 pC/N) were obtained even at poling temperatures of 70°C, for fields of 150 kV/cm.

Film breakdown occurred at temperatures above 95°C if a poling time of 30 minutes was used, with the fields shown. Significant piezoelectric activity was restricted therefore to films poled in the rather limited range of voltages and temperatures indicated by Fig. 1 (a) and (b). The poling time dependence was investigated by poling γ-phase films at 90°C with a field of 330 kV/cm for various times up to 30 minutes and this data is shown in Fig. 2. It is clear that under these conditions, most of the polarization is produced in the first 5 minutes of poling. From these results it appears that it may be possible to pole at higher temperatures and voltages, if the film is initially carefully dried and if shorter poling times are used. Since the measured values of d_{31} appear to be very sensitive to applied field and temperature at conditions just prior to dielectric breakdown, it may prove possible to obtain much higher values of d_{31}. From the data obtained from the films poled at 330 kV/cm, it can be seen that a 10°C increase in poling temperature from 90°C to 100°C would double the polarization, if dielectric breakdown had not taken place.

Fig. 3(a) and (b) shows an interesting comparison of d_{31} and e_{31} coefficients for films which were poled while in the γ-structure and those poled in the α-structure. Clearly, for equivalent poling conditions the piezoelectric activity obtained from the α-structure films is much less than that obtained from the γ-structure films. Further studies are needed to elucidate the reasons for this phenomenon. However it is clear that the crystal structure during poling is important. The α-structure is known to be a polar structure while the γ-structure was proposed as pseudo-hexagonal, with dipole orientation random and perpendicular to the chain direction(10). This latter requirement would imply a non-polar structure. This would seem to contradict the interpretation of piezoelectricity in PVF_2 where it has been shown that a polar structure is necessary for high piezoelectric activity.

In order to understand this apparent contradiction the poling mechanism should be examined more closely. In the case of PVF_2, rotation about molecular axes occurs during application of high poling fields and temperature. The energy barrier to rotation is probably quite small since only van der Waal's bonding is important in determining the lateral chain packing. 180° switching of dipoles has been suggested$^{(4)}$, which would entail chain rotations of 180°. More recently 60° rotations$^{(15)}$ have also been suggested. In the case of nylon 11, the α-phase unit cell is triclinic. The structure consists of hydrogen bonded sheets which are perpendicular to the b-axis. The influence of temperature on this structure can best be studied using x-ray diffraction, and examining the (010) and (100) reflections. The (010) reflection corresponds to the spacing between the hydrogen bonded sheets. The (100) reflection corresponds to planes perpendicular to the direction of hydrogen bonds. It is likely that the energy barrier for 180° rotation for this structure would be very high since hydrogen bonds would have to be broken and reformed.

Fig. 4 shows the change in d-spacing for (100) and (010) planes as the temperature increases. In the [010] directions the thermal expansion is typical of a van-der Waal bonded lateral packing. In the [100] direction a negative thermal expansion coefficient is observed until at 95°C both planes have the same spacing. At this point the thermal expansion perpendicular to the chains is isotropic up to melting, implying that the original hydrogen bonded sheet structure has broken up and that at temperatures above 95°C hydrogen bonds are distributed randomly about the chain direction. In the absence of poling this would imply a non-polar structure. However it is possible that for such a structure, for chains approximately perpendicular to the field direction, an alignment of dipoles in the field direction may be favored. Since at 95°C, in the absence of a field, the hydrogen bonded arrangement giving rise to the α-structure collapses to give rise to random dipole orientation, it would seem plausible that under the action of a field, dipole alignment at temperatures approaching 95°C might take place. However this temperature could not be reached without breakdown. For the case of the γ-structure, at room temperature it would appear that little dipole realignment occurs. However at higher temperatures the dipole orientation in the direction of applied field may be favored. Since the energy barrier to rotation might be expected to be less in this less well-ordered structure. Such a mechanism might be expected to give rise to structure changes for crystallites with appropriate orientation to the applied field. These changes are being studied using x-ray diffraction methods and the results will be presented as a separate publication.

The reason that previous workers did not find high d_{31} coefficients in poled nylon 11 films now seems clear. At too high a poling temperature breakdown occurs unless the applied field is extremely low, resulting in very small d_{31} coefficients. At too low a poling temperature the energy barrier to dipole realignment is too high. γ-phase films can be poled at temperatures below 95°C with high fields and without breakdown, and this results in large values for d_{31}.

Further studies are being carried out to elucidate further the mechanisms occurring during poling of nylon 11 films.

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FIGURE CAPTIONS

Figure 1 - (a) The poling temperature dependence of the piezoelectric strain coefficient, d_{31}, at different poling fields

(b) The poling temperature dependence of the piezoelectric stress coefficient, e_{31}, at different poling fields

Figure 2 - The poling time dependence of d_{31} for γ-phase Nylon 11 film poled at 330 KV/cm at 90°C

Figure 3 - (a) A comparison of the poling temperature dependence of d_{31} for Nylon 11 films containing the α-form or the γ-form

(b) A comparison of the poling temperature dependence of e_{31} for Nylon 11 films containing the α-form or the γ-form

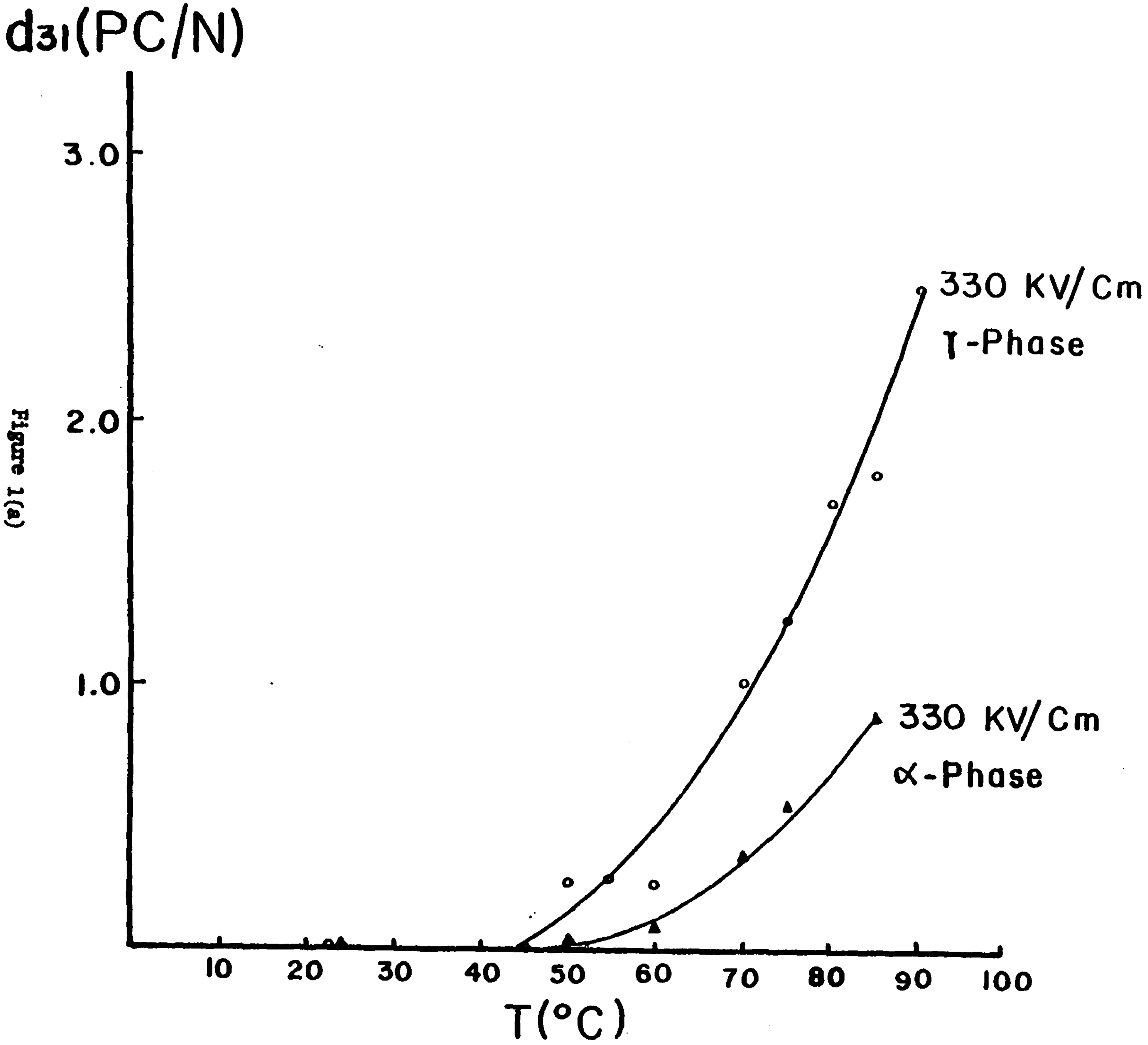
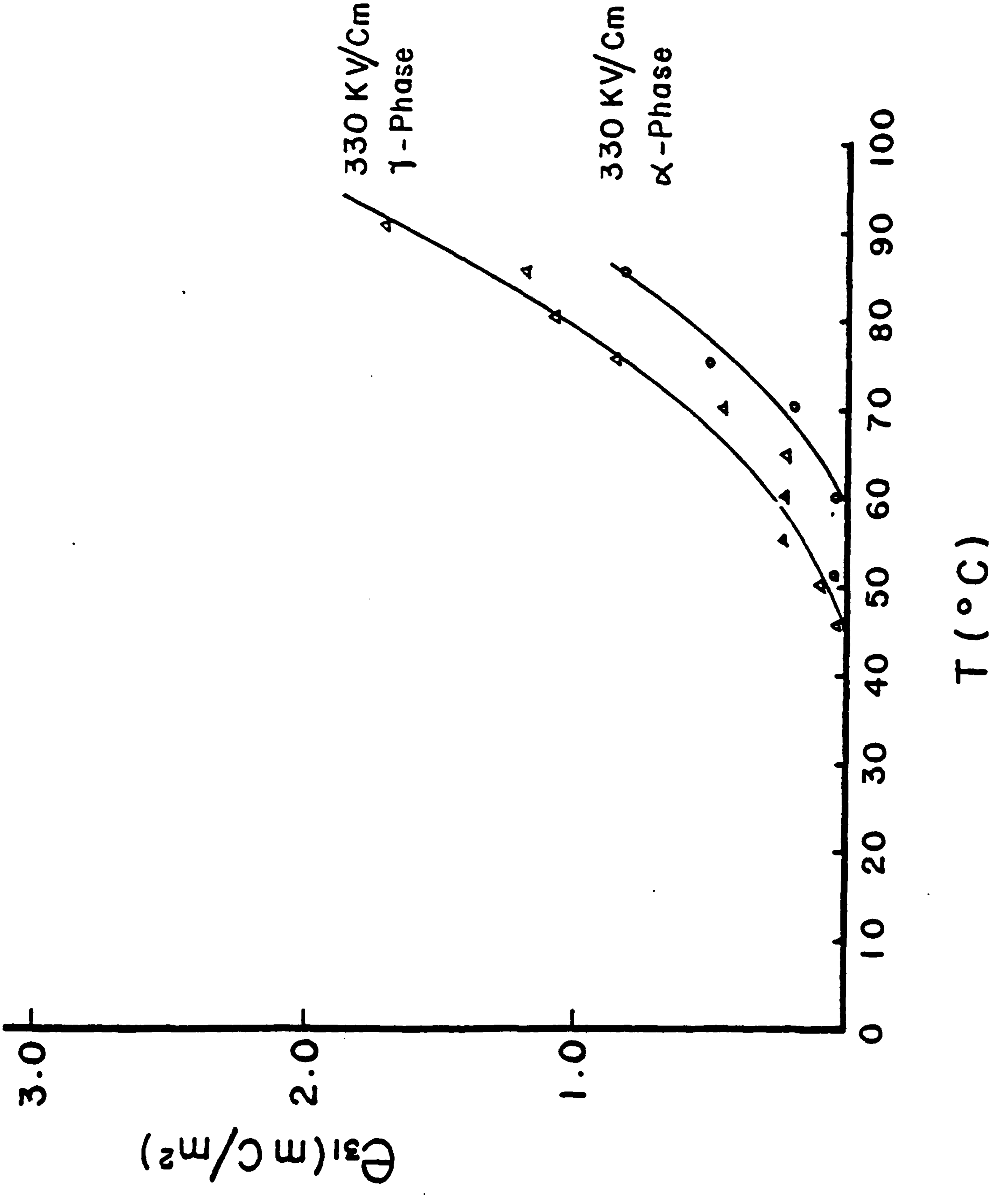
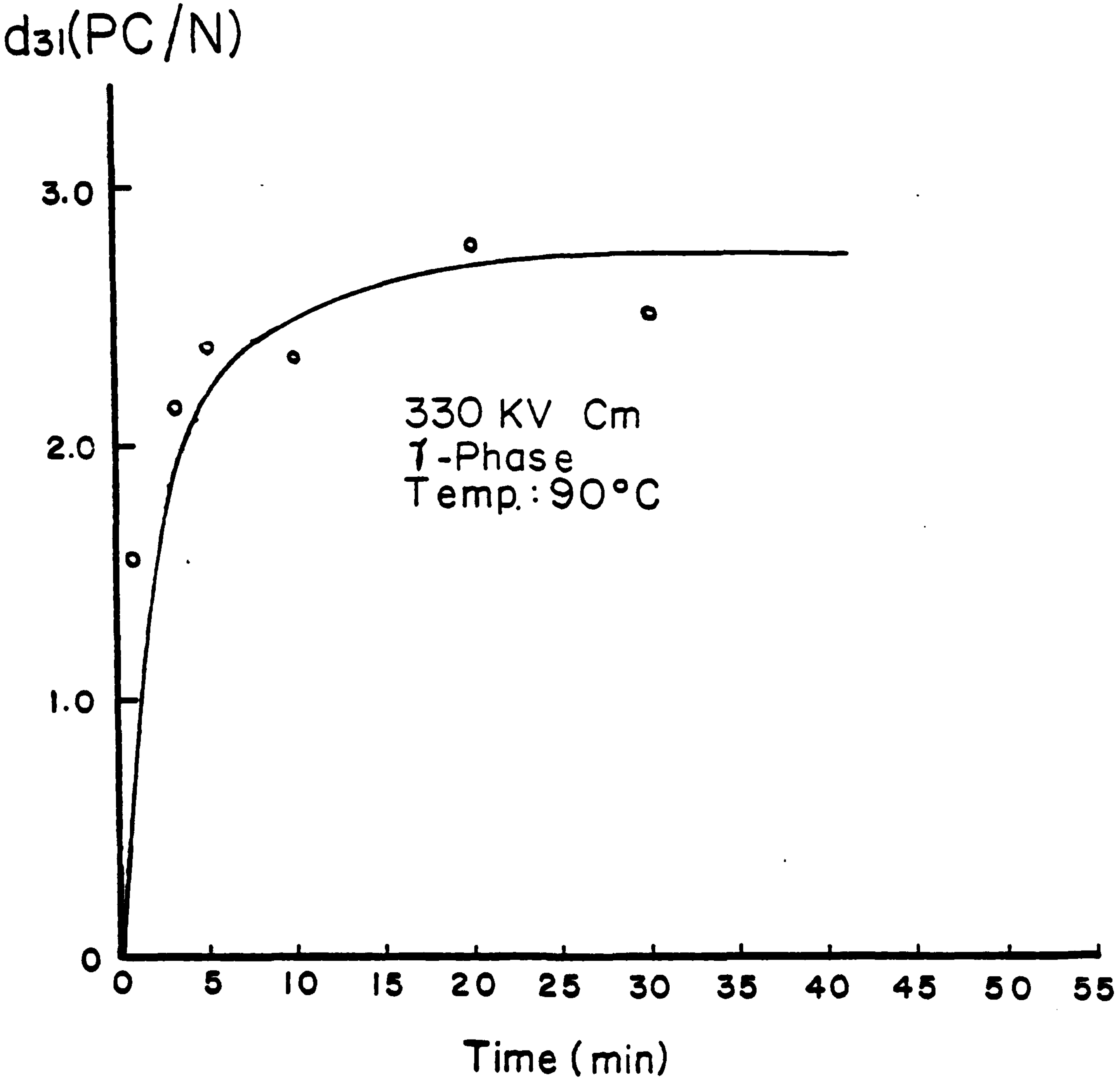

d31(PC/N)
3.0
2.0
1.0
10
20
30
40
50
60
70
80
90
100
T(°C)
330 KV/Cm
γ-Phase
330 KV/Cm
α-Phase

Figure 1(a)



330 KV/Cm
γ-Phase
330 KV/Cm
α-Phase
3.0
2.0
1.0
e_{31} (m C/m^2)
0
10
20
30
40
50
60
70
80
90
100
T (°C)

Figure 1(b)



d31(PC/N)
3.0
2.0
1.0
0
0
5
10
15
20
25
30
35
40
45
50
55
Time (min)
330 KV Cm
γ-Phase
Temp.: 90°C

Figure 2

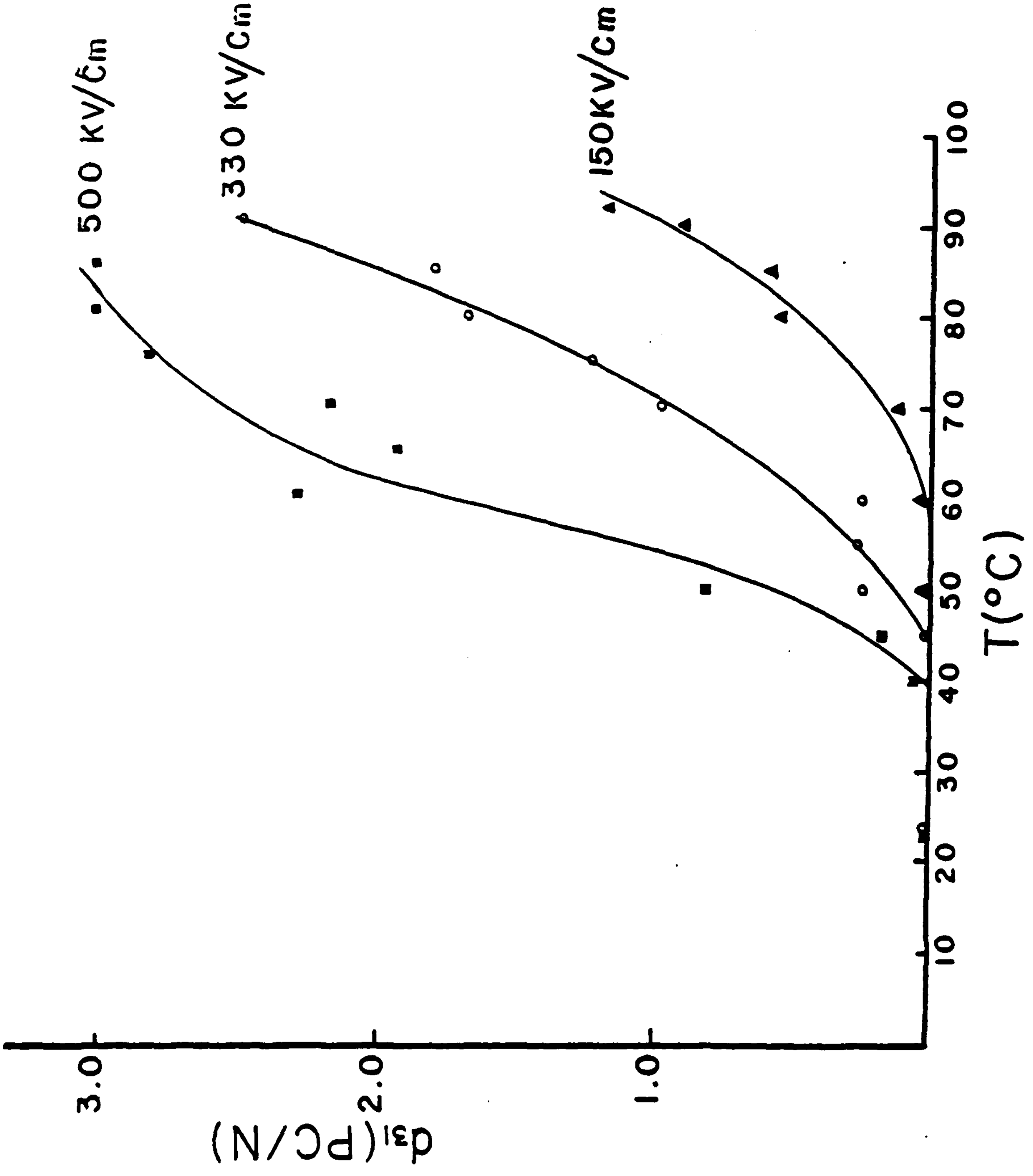

500 KV/Cm
330 KV/Cm
150KV/Cm
d_{31}(PC/N)
3.0
2.0
1.0
T(°C)
10
20
30
40
50
60
70
80
90
100

Figure 3(a)

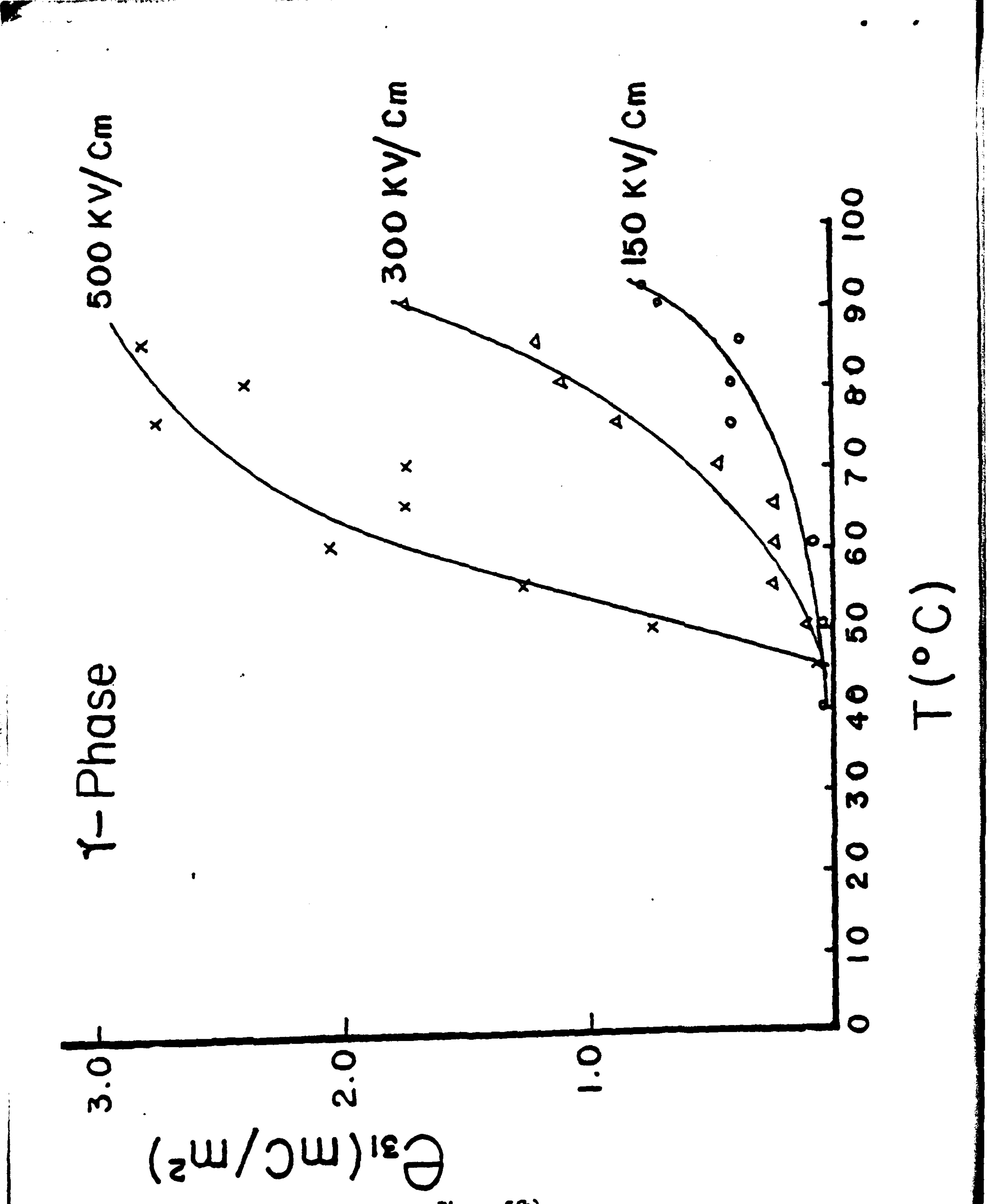

γ- Phase
500 KV/Cm
300 KV/Cm
150 KV/Cm
0
10
20
30
40
50
60
70
80
90
100
T(°C)
e_{31}(mC/m²)
3.0
2.0
1.0

Figure 3(b)