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Inverse piezoelectric effect and electrostrictive effect in polarized poly(vinylidene fluoride) films

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The piezoelectric stress coefficient and electrostriction coefficient for unpoled and poled films of polyvinylidene fluoride have been determined by applying a sinusoidal electric field and detecting stresses with the same and double frequency as the applied field, respectively. The piezoelectric coefficient shows a hysteresis with the cyclic change of the d.c. bias field. Under the poling field, the dipoles in polymers are preferentially oriented in the direction of the field, thus producing a residual polarization associated with a residual stress. Both coefficients increase with increasing temperature. A phenomenological interpretation for the piezoelectricity in poled polymers is given in terms of electrostriction and residual stress.

1. Introduction

Piezoelectricity and electrostriction in polar polymers such as polyvinylidene fluoride (PVF_2) have been studied recently by several authors [1-3]. If stretched film of polyvinylidene fluoride is subjected to a strong electric field such as 500 kV cm^{-1} at a temperature near 100° C for several hours and cooled to room temperature under the electric field, the film then becomes strongly piezoelectric [4-9]. A similar phenomenon has been observed in polar polymers other than PVF_2, such as polyvinyl fluoride and polyvinyl chloride [10-13]. Pyroelectricity and optical harmonic generation has also been observed in the drawn and poled PVF_2 [14-19]. It is generally believed that a preferential orientation of dipoles is induced in the electret film of PVF_2, which resembles the spontaneous polarization in ferroelectric crystals [7, 20-22].

The observation of the inverse piezoelectric effect in non-polar polymers such as polyethylene and polypropylene under a d.c. electric field has been also reported recently [23, 24]. In the present paper, the measurement of inverse piezoelectric effect has been carried out for the drawn and poled films of PVF_2. The electrostriction effect has also been observed for the same films. A phenomenological interpretation for the piezoelectric and electrostrictive effects in the electret films has been undertaken.

2. Experimental

Rectangular co-ordinates are assigned to the film as follows: the 1-axis is the direction of elongation, the 3-axis perpendicular to the film surface, and the 2-axis in the plane of the film. If an electric field is given in the 3 direction to a clamped film, a mechanical stress is produced in both the 1 and 2 directions. The piezoelectric stress coefficients, e_{31} and e_{32}, give the ratio of the stress to the field respectively. It has been found [5] that e_{31} is several times larger than e_{32}. In this paper we shall consider only e_{31} as the field is applied in the 3-direction and the stress detected only in the 1-direction. For the purpose of simplicity, we shall omit the suffixes showing co-ordinates in the following explanations.

The stress T in the sample is generally expressed as a function of strain S and electric field E as,

$$T = G^E S + eE + \gamma E^2 \qquad (1)$$

where G^E is the elastic coefficient at $E = 0$, e the piezoelectric stress coefficient, and γ the electrostriction coefficient. When a non-piezoelectric sample is rigidly clamped, $S = 0$, and $e = 0$, we have

$$T = \gamma E^2 . \qquad (2)$$

The constant γ is thus obtained by determining the stress T with a frequency twice that of the applied sinusoidal electric field E.

If a d.c. electric field E_0 is added as a bias field, Equation 2 becomes

$$T = \gamma(E_0 + E)^2 = \gamma E_0^2 + 2\gamma E_0 E + \gamma E^2 . \tag{3}$$

The first term represents a static stress. The second term $T(\omega)$ shows the stress with the same frequency as that of the applied field, which represents an apparent piezoelectricity. The third term $T(2\omega)$, shows the electrostriction. We can determine the electrostriction coefficient γ by measuring either the second term or the third term of Equation 3.

In the above description, we have ignored the effect of electrostatic force, which should occur between two electrodes of the sample. The electrostatic force between two parallel infinite plates is given by $\epsilon E^2/8\pi$ where ϵ is the dielectric coefficient. Using Poisson's ratio σ, the longitudinal stress in the plane of the film due to the electrostatic force is given by $\epsilon E^2\sigma/8\pi$, which has an angular frequency 2ω, if the angular frequency of E is ω. Therefore, a term of $\epsilon E^2\sigma/8\pi$ should be added to Equations 1 to 3. In order to obtain the value of γ, the correction for this term must be included.

A schematic diagram of the measuring apparatus is shown in Fig. 1. A film sample, approximately 15 × 10 × 0.05 mm^3, is fixed between two metal clamps inside a thermostat. One end is rigidly clamped and the other is connected to a piezoelectric ceramic (PZT) element. When a sinusoidal high voltage is applied between two electrodes of the sample, a sinusoidal stress in the elongated direction is detected by a PZT element, the sensitivity of which is 5.68×10^9 N C^{-1}. The output of the PZT element is amplified by a charge amplifier, passed through a filter and read with a vacuum tube voltmeter and an oscilloscope. The gain of the charge amplifier combined with the filter is calibrated by introducing a known voltage from an oscillator to the input of the charge amplifier shunted with a standard capacitor of 100 pF. The ratio of the amplitudes of the higher harmonics to the fundamental frequency in the output signal from the oscillator was less than 1%. By tuning the filter to either the same or double frequency of the voltage applied to a piezoelectric sample, the piezoelectric stress-coefficient e and the electrostriction coefficient γ are obtained from Equation 1 as follows, if the electrostatic force can be ignored:

$$e = T(\omega)/E , \tag{4}$$

$$\gamma = \sqrt{2}T(2\omega)/E^2 \tag{5}$$

where E is the mean square value of the electric field across the film with an angular frequency ω, and $T(\omega)$ and $T(2\omega)$ the mean square values of the stress in the elongated direction of the film at angular frequencies of ω and 2ω, respectively. Even when the film is not piezoelectric, if a d.c. voltage is applied to the film in superposition with a sinusoidal voltage, we may observe the apparent piezoelectricity given by the second term of Equation 3. The temperature of the sample can be varied from −170 to 200°C and the frequency of measurement can be changed from 15 to 200 Hz.

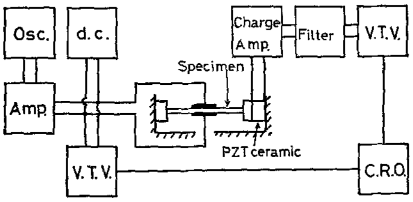

Figure 1 Schematic diagram of the experimental apparatus.

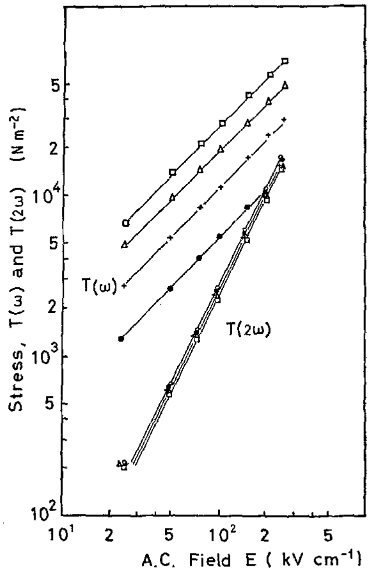

Figure 2 The stress $T(\omega)$ and $T(2\omega)$ plotted against the field $E(\omega)$ at ω = 37.5 Hz with different superposed d.c. field E_0. ○: $E_0 = 0$, ●: E_0 = 61 kV cm^{-1}, +: E_0 = 122 kV cm^{-1}, △: E_0 = 183 kV cm^{-1}, □: 244 kV cm^{-1}.

3. Electrostriction

Fig. 2 shows the observed stress $T(\omega)$ and $T(2\omega)$ for an unpoled polyvinylidene fluoride film under a sinusoidal electric field E with a frequency of 37.5 Hz superposed by various d.c. bias field E_0. The slopes of the lines indicate that $T(\omega)$ is linearly related to E and that $T(2\omega)$ is proportional to E^2.

Since this PVF_2 film is not poled, no large intrinsic piezoelectricity is expected to be observed. However, owing to the presence of a d.c. field E_0, the second term in Equation 3 gives an apparent piezoelectric effect. $e_0 = 2\gamma E_0$ is called the apparent piezoelectric stress coefficient. The coefficient of E^2 observed from the E-dependence of $T(2\omega)$ is named the apparent electrostriction coefficient γ_{obs}. γ_{obs} includes the effects of both intrinsic electrostriction and electrostatic force. The values of e_0 and γ_{obs} obtained from Fig. 2 are shown in Table I. It is seen that e_0 increases but γ_{obs} decreases with increasing d.c. field E_0. The value of γ_{obs} can be also obtained from e_0 using the relation of $e_0 = 2\gamma E_0$. This derivation was used for PVF_2 and other substances as shown in the third column of Table II, which will be described later.

TABLE I The apparent piezoelectric stress coefficients e_0 and the electrostriction coefficients γ_{obs} (observed) and γ (corrected for electrostatic force) for unpoled PVF_2 with d.c. bias field E_0. (For e, 1 MKS unit = 3 × 10^5 cgs units and for γ, 1 MKS unit = 9 × 10^9 cgs units.)

E_0 (kV cm^{-1})	e_0 (10^{-3} N(Vm)$^{-1}$) from $T(\omega)$	γ_{obs} (10^{-11} N V^{-2}) from $T(2\omega)$	γ (10^{-11} N V^{-2})
0	0	4.3	2.9
61	0.6	4.1	2.7
120	1.1	3.8	2.4
180	2.0	3.4	2.0
240	2.9	3.2	1.8

In order to investigate the electrostatic effect, similar measurements were carried out for various kinds of polymer films other than PVF_2. The apparent piezoelectric coefficient e_0 and the apparent electrostriction coefficient γ_{obs} determined under a d.c. bias of 100 kV cm^{-1} for the films of polystyrene (PS), epoxy resin, polyvinyl chloride (PVC), polymethyl methacrylate (PMMA), and poly-γ-methyl-L-glutamate (PMG) are listed in Table II. The second ($e_0 = 2\gamma E_0$) and the third ($T(2\omega) = \gamma E^2$) terms in Equation 3 can be used to determine the values of γ_{obs} and these are listed in the third and fourth columns of Table II, respectively.

TABLE II The apparent piezoelectric coefficient e_0 and the apparent electrostriction coefficient γ_{obs} under a d.c. field E_0 = 100 kV cm^{-1} for various polymer films

Polymer	e_0 (10^{-4}N(Vm)$^{-1}$) from $T(\omega)$	γ_{obs} (10^{-12} N V^{-2}) from $T(\omega)$	from $T(2\omega)$
PS	0.7	3.3	3.9
Epoxy	1.0	5.1	5.3
PVC	1.1	5.3	6.2
PMMA	1.6	8.2	5.7
PMG	2.3	12.5	8.3
PVF_2	9.4	48.0	39.0

The values of γ_{obs}, obtained from the apparent piezoelectricity using the relation $e_0 = 2\gamma E_0$, (column 3) are close to those derived from the relation $T(2\omega) = \gamma E^2$ (column 4) and range from 3 to 7 × 10^{-12} N V^{-2} except for PMG and PVF_2. These polymers show an intrinsic piezoelectricity in addition to the apparent piezoelectricity. As described above the electrostatic stress is given by $(\epsilon\sigma/8\pi)E^2$. If we assume $\epsilon = 4$, $\sigma = 0.35$, we get $\epsilon\sigma/8\pi = 6 \times 10^{-12}$ N V^{-2} which is in the range of γ_{obs} given above. Therefore, the values of γ_{obs} shown in the third and fourth columns of Table II, except for PMG and PVF_2, should mainly come from the electrostatic force.

For PMG and PVF_2, γ_{obs} derived from e_0 is significantly larger than γ_{obs} derived from $T(2\omega)$. This suggests that PMG and PVF_2 have intrinsic piezoelectricity in addition to apparent piezoelectricity. Perfectly unpoled PVF_2 should have no intrinsic piezoelectricity. However, residual polarization present in the specimen may cause piezoelectricity to the small extent shown in Table II. Values of γ_{obs} obtained from $T(\omega)$ are greater than those from $T(2\omega)$ for PMG, suggesting that intrinsic piezoelectricity also exists in PMG films [2].

The electrostriction coefficient for PVF_2 should also be corrected for the effect of electrostatic force. At room temperature, $\epsilon\sigma/8\pi$ for PVF_2 is 1.4 × 10^{-11} N V^{-2}, while γ_{obs} in Table II is 3.9 × 10^{-11} N V^{-2} at an electric field of 100 kV cm^{-1}. By subtracting the former from the latter, we obtain the correct value of 2.5 × 10^{-11} N V^{-2} for the electrostriction coefficient γ. Table I also includes corrected values of γ in column 4.

4. Piezoelectricity

A large intrinsic piezoelectricity is observed for drawn and poled films of PVF_2. However, as described above, the apparent piezoelectricity is

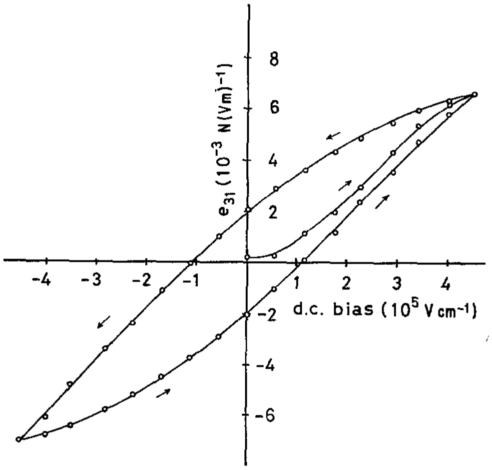

Figure 3 The piezoelectric stress-coefficient e_{31} for an unpoled film of PVF_2 plotted against the cyclic change of the d.c. bias field E_0.

also observed for the unpoled film under a d.c. bias field. Fig. 3 shows the apparent piezoelectric stress-coefficient e_0 of an unpoled film of PVF_2, measured at 25°C with a frequency of 37.5 Hz, as a function of d.c. bias field. The magnitude of applied a.c. field was 90 kV cm^{-1}. With the cyclic change of the bias field, e_0 showed a marked hysteresis curve. Even at room temperature, once subjected to a high d.c. field, the film shows intrinsic piezoelectricity after the d.c. field is removed. In this state it is most likely that a residual polarization remains in the sample, similar to ferroelectric crystals.

Fig. 4 illustrates e plotted against the cyclic change of the d.c. bias field for a rolled and poled PVF_2 film which has been polarized at 80°C for 6 h under a d.c. field of 340 kV cm^{-1}. The measurements were carried out at room temperature with an a.c. field of 68 kV cm^{-1} at 30 Hz. Since the film has been poled, piezoelectricity is observed even with no d.c. bias field. A hysteresis curve similar to that in Fig. 3 is clearly seen. This figure shows that the residual field is 450 kV cm^{-1}.

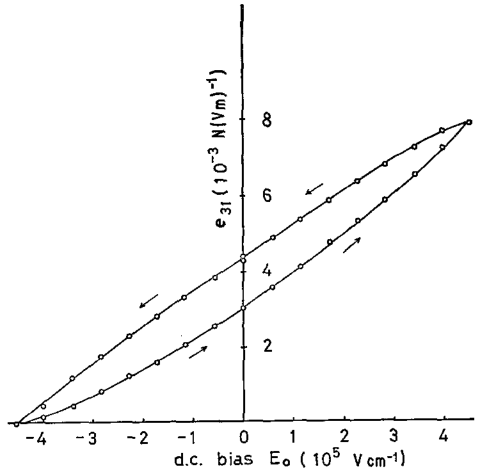

Figure 4 The piezoelectric stress-coefficient e_{31} for a rolled and poled film of PVF_2 plotted against the cyclic change of the d.c. bias field E_0.

The temperature dependence of e and γ for a poled sample with no d.c bias field is shown in Fig. 5. The values of e and γ increase with rising temperature. Their decrease above 50°C may be due to the depolarization of the poled film.

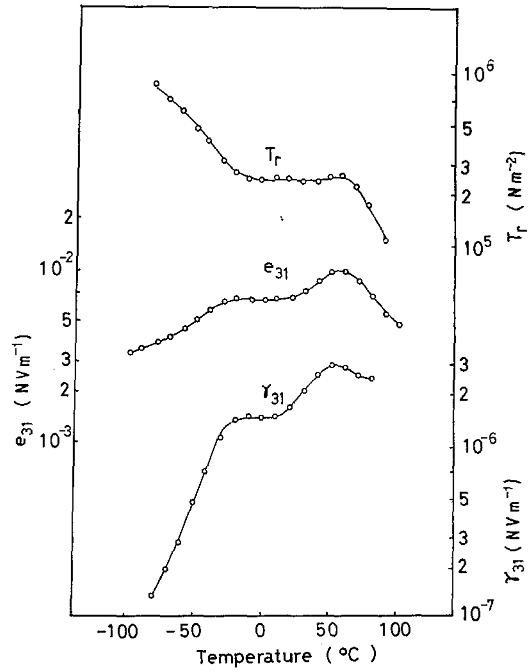

Figure 5 The temperature dependence of the piezoelectric stress coefficient e_{31}, the electrostriction coefficient γ_{31}, and the residual stress T_r for a drawn and poled film of PVF_2.

If the e-coefficient is measured continuously during the period of the poling process, a gradual increase of e is observed as shown in Fig. 6. The sample is maintained at 80°C under a d.c. field of 380 kV cm^{-1}. The value of e increases slowly and levels off after about 4 h. On the other hand, the electrostriction coefficient, γ decreases slightly during the poling process.

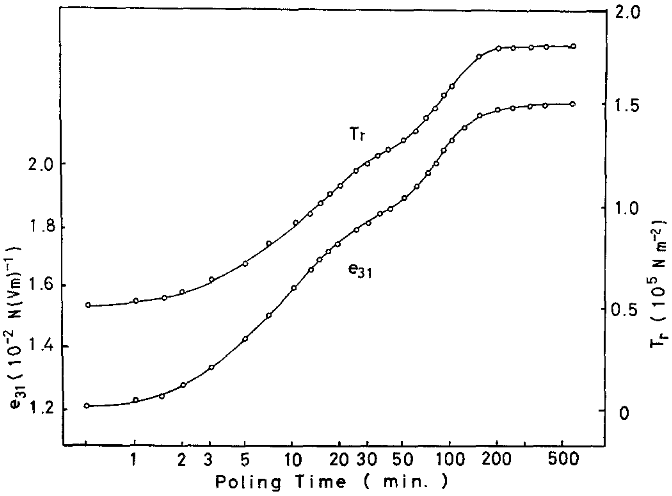

Figure 6 The increase of the piezoelectric stress coefficient e_{31} and the residual stress T_r for a PVF$_2$ film during the poling process at 80° C under 380 kV cm^{-1}.

5. Discussions

Piezoelectricity is observed without applying a d.c. bias field for rolled and poled films of PVF$_2$. Apparent piezoelectricity is also observed for unpoled films of PVF$_2$ with a d.c. bias field. The latter can be explained by the coupling of the electrostriction and the d.c. bias field as shown in Equation 3. We assume that the piezoelectricity for poled PVF$_2$ can be also interpreted in terms of electrostriction. After poling, a prefered orientation of dipoles is produced in the film, which results in the residual stress T_r and the residual field E_r. The coupling of the electrostriction with this residual stress may produce piezoelectricity.

In phenomenological expression, the stress T in the poled film of PVF$_2$ under an electric field E is given at the clamped condition ($S = 0$) by

$$T = T_r + eE + \gamma E^2 . \qquad (6)$$

Then, in analogy with Equation 3 we may write

$$T_r = \gamma E_r^2 \qquad (7)$$

and

$$e = 2\gamma E_r , \qquad (8)$$

where T_r is the residual stress, e is the piezoelectric stress-coefficient, and E_r is the residual field caused by the residual polarization P_r.

During the poling process, the dipoles of CF$_2$ in the molecular chains are preferentially oriented in the direction of applied field, i.e. perpendicular to the film surface. When the film is cooled to room temperature under the electric field, this orientation of dipoles is retained and the oriented polar structure is permanently stabilized.

The resulting residual polarization P_r produces the residual electric field E_r according to the following relation,

$$E_r = 4\pi P_r/(\epsilon - 1) . \qquad (9)$$

For the film shown in Fig. 4, it was found that $E_r = 450$ kV cm^{-1}. If we assume $\epsilon = 10$ at room temperature, using Equation 9 we have $P_r = 3.5 \times 10^{-7}$ C cm^{-2}.

From Equations 7 and 8 we obtain

$$T_r = e^2/4\gamma . \qquad (10)$$

The values of T_r calculated from e and γ are plotted against temperature in Fig. 5. It is seen that T_r decreases until about − 20° C, where the glass transition takes place. This may be due to the increase of the amplitude of the thermal vibration of oriented dipoles.

During the poling process, the orientation of dipoles proceeds gradually with time, which induces the residual stress. It is seen in Fig. 6 that the residual stress T_r increases with time similar to the e coefficient.

It is shown in Fig. 3 that the apparent piezoelectricity is observed at room temperature for unpoled PVF$_2$ films if a d.c. field is applied. From Equation 3 the static stress $T_0 = \gamma E_0^2$ is defined similar to the residual stress T_r in the poled polymers. The values T_0 calculated by the relation $T_0 = e^2/4\gamma$ are shown in Fig. 7 for the cyclic change of the d.c. field. A butterfly figure corresponding to the hysteresis in Fig. 3 is observed. This may indicate that even at room temperature the reorientation of dipoles takes place and the residual stress is produced during the application of the bias electric field.

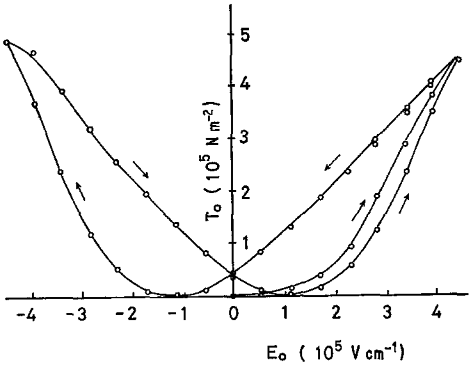

Figure 7 The stress T_0 plotted against the cyclic change of the d.c. field E_0 for an unpoled PVF_2 film.

On the other hand, in polymers shown in Table II such as PS, Epoxy, PVC and PMMA, the apparent piezoelectric effect and the apparent electrostrictive effect are both due to the electrostatic force, because the values of γ_{obs} derived from either the apparent piezoelectric coefficient e_0 or the stress $T(2\omega)$ are almost the same as that calculated from the electrostatic force.

6. Conclusions

The apparent inverse piezoelectric effect has been observed for unpoled poly(vinylidene fluoride) films with a d.c. bias field. It can be explained by the coupling of the electrostriction of the film with the d.c. field. In analogy with this observation, the intrinsic piezoelectric effect in poled PVF_2 films may be interpreted as a consequence of the combination of the electrostrictive effect and the residual polarization (or electric field) in the poled films. During the poling process, the residual polarization accompanied by the residual stress is gradually produced by the field-induced orientation of dipoles.

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References

1. R. HAYAKAWA and Y. WADA, *Adv. Polymer Sci.* **11** (1973) 1.
2. E. FUKADA, *Prog. Polymer Sci. Japan* **2** (1971) 329.
3. *Idem*, in "Electrets" (edited by M. M. Perlman) (The Electrochemical Society, 1973) p. 486.
4. H. KAWAI, *Japan J. Appl. Phys.* **8** (1969) 975.
5. E. FUKADA and S. TAKASHITA, *ibid* **8** (1969) 960.
6. E. FUKADA and T. SAKURAI, *Polymer J.* **2** (1971) 656.
7. K. NAKAMURA and Y. WADA, *J. Polymer Sci. A-2* **9** (1971) 161.
8. J. COHEN, S. EDELMAN and C. F. VEZZETTI, in "Electrets" (edited by M. M. Perlman) (The Electrochemical Society, 1973) p. 505.
9. T. TAKAMATSU and E. FUKADA, *ibid*, p. 128.
10. S. EDELMAN, L. R. GRISHAM, S. C. ROTH and J. COHEN, *J. Acous. Soc. Amer.* **48** (1970) 1040.
11. J. COHEN and S. EDELMAN, *J. Appl. Phys.* **42** (1971) 893.
12. E. FUKADA and K. NISHIYAMA, *Japan J. Appl. Phys.* **11** (1972) 36.
13. M. G. BROADHURST, C. G. MALMBERG, F. I. MOPSIK and W. P. HARRIS, in "Electrets" (edited by M. M. Perlman) (The Electrochemical Society, 1973) p. 472.
14. J. COHEN, S. EDELMAN and C. F. VEZZETTI, *Nature Phys. Sci.* **233** (1971) 12.
15. J. G. BERGMAN, JUN, J. H. MCFEE and G. R. CRANE, *Appl. Phys. Letters* **18** (1971) 203.
16. R. J. PHELAN, JUN, R. H. MAHLER and A. R. COOK, *ibid* **19** (1971) 337.
17. A. M. GLASS, J. H. MCFEE and J. G. BERGMAN, JUN, *J. Appl. Phys.* **42** (1971) 5219.
18. J. H. MCFEE, J. G. BERGMAN, JUN and G. R. CRANE, *Ferroelectrics* **3** (1972) 305.
19. G. PFISTER, M. ABKOWITZ and R. G. CRYSTAL, *J. Appl. Phys.* **44** (1973) 2064.
20. J. B. LANDO and W. W. DOLL, *J. Macromol. Sci. Phys.* **B2(2)** (1968) 205.
21. J. P. LUONGO, *J. Polymer Sci. A-2* **10** (1972) 1119.
22. E. W. ASLAKSEN, *J. Chem. Phys.* **57** (1972) 2358.
23. R. W. GREAVES and D. R. LAMB, *J. Mater. Sci.* **6** (1971) 74.
24. G. DREYFUS and J. LEWINER, in "Electrets" (edited by M. M. Perlman) (The Electrochemical Society, 1973) p. 517.

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