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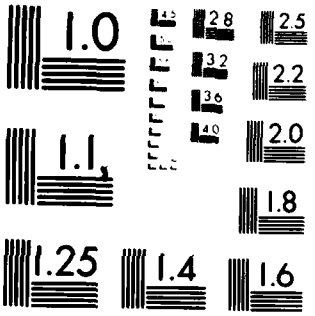

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RIGOROUS BOUNDS FOR THE CALCULATED DIELECTRIC CONSTANTS OF FERROELECTRIC POLYMERS

MARTIN G. BROADHURST
National Bureau of Standards, Washington, D.C. 20234

Abstract — A theory is presented for calculating rigorous upper and lower bounds for the dielectric constant of a semi-crystalline polymer in terms of the volume fraction of crystalline phase, the dielectric constant of the liquid phase and the anisotropic dielectric tensor of the crystalline phase. Also required are two orientation functions $\langle\cos^2\theta\rangle$ and $\langle\cos^2\alpha\rangle$ where θ defines the tilt of crystal lamellae and α the orientation of the electric moment of each crystal with respect to the measuring field. Bounds are presented for polyvinylidene fluoride for a variety of orientations.

INTRODUCTION

The dielectric constants of polyvinylidene fluoride (PVDF) and related ferroelectric polymers and copolymers are of interest in several ways. PVDF has been used for dielectric films in capacitors since long before its ferroelectric properties were recognized. For capacitors, a high-ε dielectric is desirable for reducing capacitor size and cost. (Throughout this paper we use ε to mean the dielectric constant of a film measured at audio frequencies normal to the larger film surface). The ε of PVDF is important also in some piezoelectric and pyroelectric applications such as hydrophones and vidicon elements where decreased ε means increased voltage sensitivity.

Being able to control ε is often desirable. It has long been recognized that drawing (stretching) a PVDF film raises its ε and, partly for this reason, PVDF capacitor films are usually either uniaxially or biaxially drawn. Recently, interesting butterfly-shaped dielectric-hysteresis patterns, such as the one shown in Figure 1, have been observed[1]. Here, ε is measured at 10 Hz while the electric field is cycled at 3×10^{-4} to 10^{-2} Hz between ±6kV. These data show that poling also significantly affects ε.

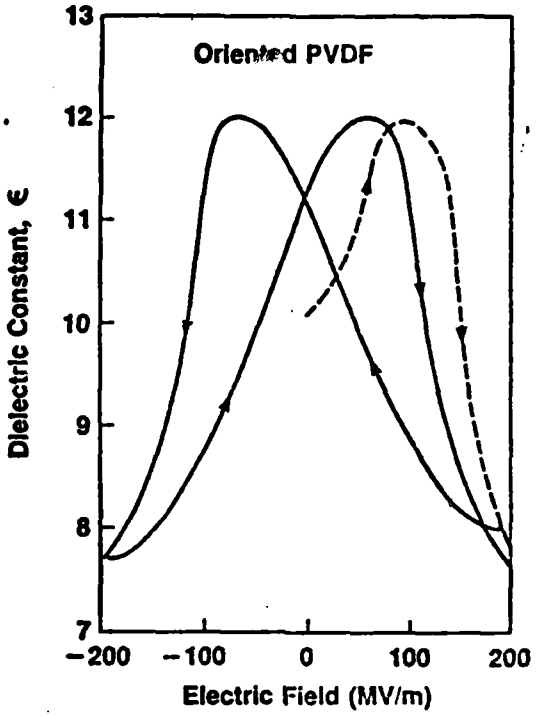

FIGURE 1. Room temperature dielectric hysteresis of 6 μm, mostly β phase PVDF film drawn by rolling to 5 times the original length.[1]

Two early models to explain the increase of ε of PVDF with drawing have been proposed. The first model[2] emphasizes the role of the liquid phase. The molecules are assumed to orient preferentially in the draw direction, so that rotation of the dipoles about the long molecular axis provides an increased contribution to ε. A second model[3] considers orientation of stacks of crystal and amorphous lamellae. In this model drawing aligns the lamellae normal to the draw direction and thereby increases the electric field in the phase of highest ε. Both models account for an increase in ε with drawing. Most researchers have assumed that the liquid phase has the higher ε. In this paper I will develop more completely the model of oriented liquid-crystal lamellae. This model has a better chance than does the oriented liquid model, of accounting for the dependence of ε on poling, since the

remnant polarization most probably resides in the crystalline phase[5-8]. I will also present evidence that the highest dielectric constant comes from one direction in the crystalline phase.

An important detailed treatment of the ε of the liquid-crystal-lamellae model has been published recently by Boyd[4]. He assumed the basic morphology of semicrystalline polymers is thin lamellar crystals separated by thin layers of liquid polymer. He considered the ε to be isotropic in both phases. He obtained tight and rigorous upper and lower bounds for ε in three orthogonal directions in terms of a single orientation function $\langle\cos^2\theta\rangle$ where θ is the angle of tilt of the normal of the lamellar stacks with respect to a reference direction. Here I will modify the theory to account for anisotropic crystalline lamellae. This extension introduces one additional orientation function $\langle\cos^2\alpha\rangle$ where α is the angle between the direction ε is measured and the electric moments of the crystals. Six orientation functions must be provided to obtain ε in three orthogonal directions.

THEORY

We assume that PVDF has a morphology typical of semicrystalline polymers as shown in Figure 2.

The crystals are shown in a polar, chain-folded orthorhombic crystal phase with different crystal ε's, ε_c, in the x', y' and z' directions. The liquid is assumed isotropic with $\varepsilon=\varepsilon_l$. The x', y' and z' axes correspond respectively to the direction of the electric moment, the direction normal to both the moment and molecular chain and the direction normal to the crystal lamellae. This structure is a reasonable approximation to any of the polar phases of PVDF.

We now fix a new coordinate system x, y, z in a sample as shown in Figure 3.

The upper, ε_U, and lower bounds ε_L, for ε are derived from assuming respectively a uniform electric field $\underline{E}$ and a uniform

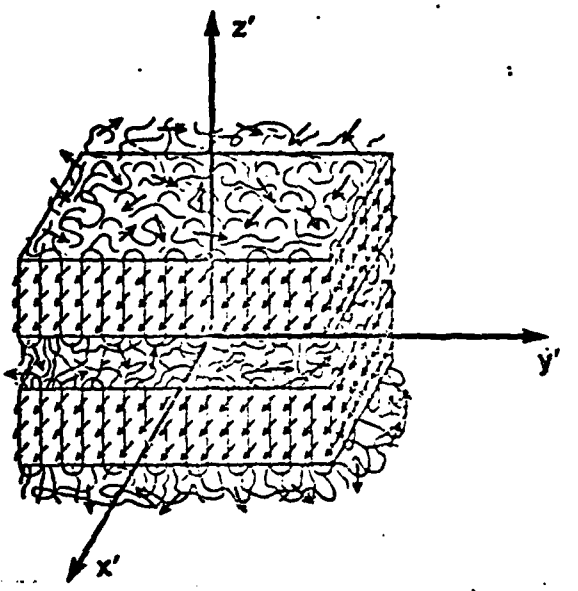

FIGURE 2. Assumed morphology and coordinates of a stack of liquid and crystal lamellae

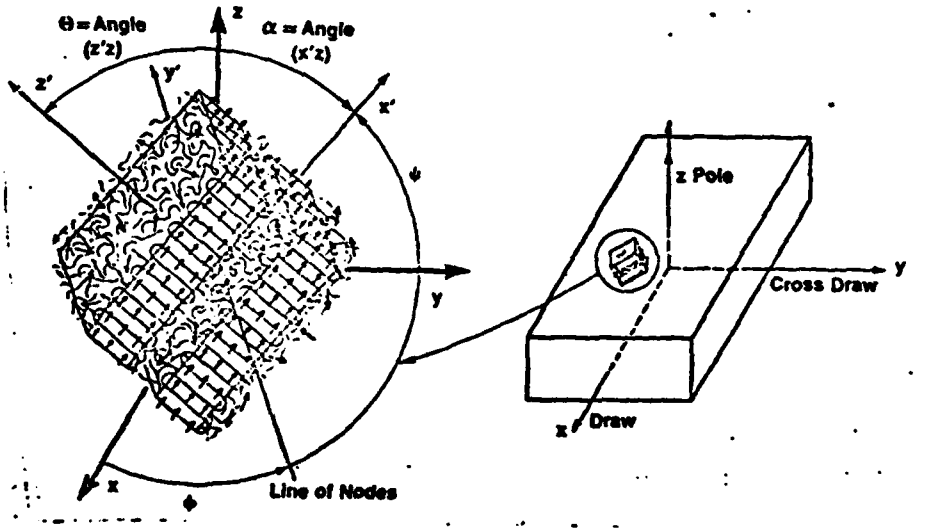

FIGURE 3. Sample-centered coordinate system and orthogonal transformation angles for an arbitrarily oriented liquid-crystal stack

electric displacement $\underline{D}$ throughout the sample. These bounds are[4]

$$\epsilon_U = \underline{E}^T (\underline{\underline{T}}\underline{\underline{\epsilon}}\underline{\underline{T}}^{-1})\underline{E}/E_o^2 \tag{1}$$

$$\epsilon_L = \underline{D}^T (\underline{\underline{T}}\underline{\underline{\epsilon}}^{-1}\underline{\underline{T}}^{-1})\underline{D}/D_o^2 \tag{2}$$

We are concerned here with the ϵ in the z direction only so we choose

$$\underline{E} = \begin{pmatrix} o \\ o \\ E \end{pmatrix}, \text{ and } \underline{D} = \begin{pmatrix} o \\ o \\ D \end{pmatrix}. \tag{3}$$

$\underline{E}^T$ and $\underline{D}^T$ are the transposed vectors of $\underline{E}$ and $\underline{D}$, and E_o and D_o are their magnitudes. The dielectric tensors for the stack are

$$\epsilon_S = \begin{pmatrix} \epsilon_S(x') & o & o \\ o & \epsilon_S(y') & o \\ o & o & \epsilon_S(z') \end{pmatrix} \tag{4}$$

and

$$\epsilon_S^{-1} = \begin{pmatrix} \epsilon_S^{-1}(x') & o & o \\ o & \epsilon_S^{-1}(y') & o \\ o & o & \epsilon_S^{-1}(z') \end{pmatrix} \tag{5}$$

$\underline{\underline{T}}$ is an orthogonal rotational transformation matrix which transforms a vector in the x', y', z' coordinate system to one in the x, y, z coordinate system. I used the transformation matrix given by Goldstein[9],

$$T = \begin{pmatrix} \cos\psi\cos\phi - \cos\theta\sin\phi\sin\psi & -\sin\psi\cos\phi - \cos\theta\sin\phi\cos\psi & \sin\theta\sin\phi \\ \cos\psi\sin\phi + \cos\theta\cos\phi\sin\psi & -\sin\psi\sin\phi + \cos\theta\cos\phi\cos\psi & -\sin\theta\cos\phi \\ \sin\theta\sin\psi & \sin\theta\cos\psi & \cos\theta \end{pmatrix} \tag{6}$$

The results of evaluating Eqs. (1) and (2) are:

$$\epsilon_U = (1-A-B)\epsilon_S(x') + B\epsilon_S(y') + A\epsilon_S(z') \tag{7}$$

$$\epsilon_L = 1/[(1-A-B)/\epsilon_S(x') + B/\epsilon_S(y') + A/\epsilon_S(z')] \tag{8}$$

where

$$A = \langle\cos^2(z'z)\rangle = \langle\cos^2\theta\rangle \tag{9}$$

$$B = \langle\cos^2(x'z)\rangle = \langle(\sin\theta\cos\psi)^2\rangle = \langle\cos^2\alpha\rangle \tag{10}$$

$$\epsilon_S(x') = (1-V)\epsilon_1 + V\epsilon_c(x') \tag{11}$$

$$\epsilon_s(y') = (1-V)\epsilon_1 + V\epsilon_c(y') \quad (12)$$

$$\epsilon_s(z') = 1/[(1-V)/\epsilon_1 + V/\epsilon_c(z')] \quad (13)$$

where V is the volume fraction of crystals.

We now need values for ϵ_1 and the ϵ_c's. Consider the case of β-phase PVDF where the CH_2-CF_2 dipole moment is normal to the molecular chain axis. Librational motions of the dipole about the chain axis contribute to ε in the y'/direction. The ε of such a harmonic librator is given by,

$$\epsilon = 1 + Nm^2\langle\psi_T^2\rangle/2\epsilon_o kT \quad (14)$$

where for β phase PVDF $Nm = 0.2\ Cm^{-2}$ is the remnant dipole moment per unit volume[10], $\langle\psi_T^2\rangle^{1/2} = 16°$ is the root mean squared librational amplitude[10] at T = 300K, $m = 117 \times 10^{-30}$ Cm (equivalent to 10 CH_2-CF_2 dipoles)[11] is the dipole moment of an effectively independently librating molecular segment, k is Boltzmanns constant and ϵ_o the permittivity of free space. From Eq. (14) we find $\epsilon_c(y') = 25$. $\epsilon_c(x') \simeq \epsilon_c(z') \simeq 3$ are chosen because they result primarily from atomic and electronic displacement polarization. $\epsilon_1 = 12$ from an ε-vs-temperature extrapolation of ε measured above the melting point[12]. We use a typical crystal-volume-fraction of V=0.5.

For sample calculations, we consider films whose state of polarization is specified by $\langle\cos^2\psi\rangle$ (see Figure 3). For an unpoled sample $\langle\cos^2\psi\rangle = \langle\sin^2\psi\rangle = 1/2$. For a sample poled as much as possible in the z direction, $\langle\cos^2\psi\rangle = 0$ and for one poled as much as possible in the x-y plane, $\langle\cos^2\psi\rangle = 1$. For these three limiting cases, ψ and θ are uncorrelated and we can use $B \equiv \langle(\sin\theta\cos\psi)^2\rangle = \langle\sin^2\theta\rangle\langle\cos^2\psi\rangle$ or $B = (1-A)\langle\cos^2\psi\rangle$. In general, one cannot assume that θ and ψ are uncorrelated and must avoid this simplification.

RESULTS

The results of the calculation are summarized in Figure 4. The upper and lower bounds on ε are shown as a function of $\langle\cos^2\theta\rangle$

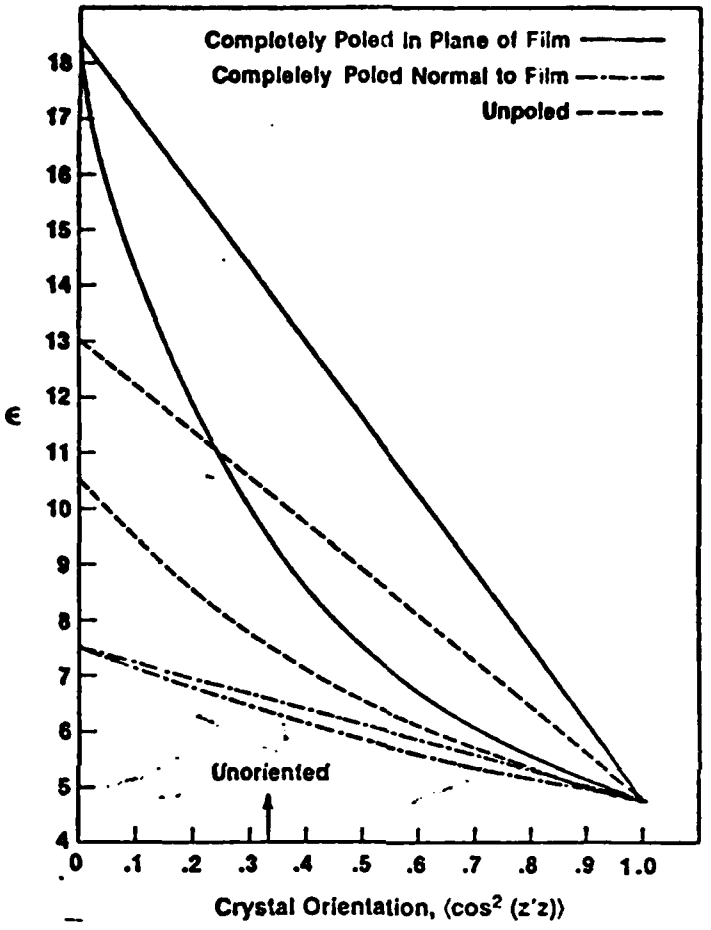

FIGURE 4. Upper and lower bounds on ε as a function of orientation for PVDF films in different states of polarization

for the three examples given above. $\langle\cos^2\theta\rangle = 1/3$ for an unoriented sample. $\langle\cos^2\theta\rangle < 1/3$ means the lamellae are preferentially aligned parallel to the z axis and $\langle\cos^2\theta\rangle >> 1/3$ means the lamellae are preferentially aligned parallel with the x-y plane of the film.

DISCUSSION

The results of our analysis are extremely interesting in the following ways:

1. We now have a quantitative evaluation of a model for ε of a ferroelectric semicrystalline polymer and calculated values of ε for films of PVDF in various states of crystal orientation and polarization. The calculated values of ε are in good accord with observed data.
2. We can see the limits of ε that can be achieved by controlling orientation, polarization and crystallinity. We see what conditions must be met to achieve high, low or intermediate values of ε and what sacrifice must be made for example in polarization to achieve a particular ε. We can better relate ε to processing variables such as draw ratio and applied poling fields.
3. We can use the results to better understand the ε hysteresis of Figure 1 and hence the polarization process in PVDF. In this case, we see that cycling the poling field causes the electric moments to align strongly in the direction of the field at large fields and slightly in the plane of the film at values of field just below the coercive field.
4. We can use the theory to determine the crystal dielectric tensor and the liquid dielectric constant of semicrystalline polymers from orientation functions and the ε's measured for semicrystalline films of the polymer. This knowledge is of considerable value in analyzing dielectric relaxation strengths and shapes to obtain their source (liquid or crystalline) and their orientation.
5. The analysis extends Boyds treatment[4] to anisotropic crystals without significantly increasing the complexity of the calculations.

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