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Kink propagation as a model for poling in poly(vinylidene fluoride)

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The poling process in β-phase poly(vinylidene fluoride) is studied in two models in which the reorientation of the electric polarization of a crystallite occurs through the propagation of a solitary wave, or kink, of rotation along the chain. While a model considered by Aslaksen, in which the rotation is through 180°, does not provide agreement with experiment, a model by Kepler and Anderson, in which the rotation is through 60°, yields results not inconsistent with observed poling times.

I. INTRODUCTION

There is currently considerable scientific and technological interest in the piezoelectric and pyroelectric properties[1] of β-phase poly(vinylidene fluoride), or PVF_2. In order to prepare this material in such a way that it exhibits these electric effects, it is first necessary to prepare electrically inactive β-PVF_2, and then subject the sample to large and enduring electric fields. This paper discusses this nonequilibrium process, known as poling.

Although there is still controversy about the origin of the electric effects[2] in β-PVF_2, it is widely believed[3] that they are a result of alignment of the electric polarizations of local crystallites within a macroscopic sample. The poling process is then a process of realignment of the crystallite polarizations. Before poling has taken place the distribution of directions of polarization of individual crystallites is random, whereas afterwards the polarization directions have a biased distribution in space, and are biased toward the direction of the applied electric field.

In this paper we study in detail two possible models for the poling process. The first was introduced by Aslaksen,[4] and involves a rotation by 180° of each chain about its axis. The second model is a more recent suggestion by Kepler and Anderson,[1] who noticed that a rotation by 60° might also occur. The discussion that follows is an attempt to explore the consequences of each of these models by developing predictions of the experimental behavior in the poling process. A preliminary account of part of this work has already appeared.[5]

In the following section the 180° model is described and solved in certain limits by an analytical approximation. In Sec. III a computer experiment is reported that yields numerical solutions to the intractable Langevin equation, and these are compared with experiment. Section IV introduces the 60° model and reports the numerical consequences of this mechanism, which are compared with the previous results in the concluding Sec. V.

II. THE 180° MODEL

The polymer backbone in β-PVF_2 has all segments in the *trans* conformation, while in α-PVF_2 the *trans* conformation alternates with *gauche* and *gauche'* conformations. As has been noted elsewhere,[6] it is thus reasonable to consider that alternate torsional angles suffer only small excursions from zero, while the intervening torsional angles are more to be considered as "soft" variables capable of taking on large values. Such an approach has been successful[6] in understanding the phase diagram of PVF_2. In this spirit the backbone chain of the β-phase material is described in terms of the angles θ_i of rotation of CF_2–CH_2–CF_2 units from the plane of the crystalline b axis ("torsional angles"). A phenomenological Hamiltonian may then be proposed of the form

$$H = T + U ,$$

where

$$T = \tfrac{1}{2} I \sum_i \dot{\theta}_i^2 \tag{1}$$

and

$$U = \sum_i [A_1(1-\cos\theta_i) + A_2(1-\cos 2\theta_i) + \tfrac{1}{2}k(\theta_i - \theta_{i+1})^2] , \tag{2}$$

where I is the moment of inertia of a monomer unit about the center-of-mass axis of the chain, and the dot signifies differentiation with respect to time. The first two terms in U represent the combined influence of the local crystalline order (that is, the interchain potential) and an applied electric field. They constitute a potential having minima at $\theta = 0$ and π, providing $4A_2 > |A_1|$. In practice, even with large applied electric fields, this condition is satisfied. The last term in U represents the torsional rigidity of the chain. The interchain potential for a monomer unit of a chain at the center of the β-phase unit cell is shown as a function of the rotational angle θ about its axis in Fig. 1.

The time variation of J_i, the angular momentum of the ith unit, defined as

$$J_i = I\dot{\theta}_i \tag{3}$$

obeys a Langevin equation[7] of the form

$$\dot{J}_i = -\partial U/\partial\theta_i - \lambda J_i + F_i(t)\,. \tag{4}$$

This equation is the dynamical equation of the system supplemented by a damping term $-\lambda J_i$ and a random term $F_i(t)$. The parameter λ is a phenomenological viscosity which represents the effect of the interchain interactions in carrying away energy from an individual chain. The term $F_i(t)$ represents the random fluctuations in forces due to thermal motion of the rest of the polymer at temperature T. In order that the Langevin equation lead to the correct equilibrium statistical mechanics for the chain, we must stipulate that

$$\langle F_i(t)\rangle = 0\,, \tag{5}$$

$$\langle F_i(t)F_j(t')\rangle = 2I\lambda k_B T\delta_{ij}\delta(t-t')\,, \tag{6}$$

where the angular brackets imply a time average and k_B is Boltzmann's constant.

Aslaksen[4] pointed out that any polymer chain in the crystal field of its neighbors had two locally stable orientations, in one of which, the stable orientation, the polarization of the chain was parallel to that of its neighbors, and in the other of which it was antiparallel to the neighbors' orientation. For this reason he suggested that poling involved a possible reversal of orientation of the polarization of a crystallite, rather than wholesale rotations of crystallites. The poling field would then lower the energy of the metastable antiparallel orientation of the chain polarizations in such a way as eventually to reverse the orientations of all polymer chains within a crystallite. The advantage of this picture is that the topological structure of a polymer sample is preserved, and large-scale motions of polymer chains, corresponding to changes of orientation of the local crystal axes, are avoided.

In this section we adopt the above picture of the poling process. For simplicity we shall consider a chain whose initial direction of polarization is in the direction $\theta = 0$ and subject to a strong poling field $-E$. The conformation of lowest energy then has the chain polarizations oriented in the direction $\theta = \pi$. An individual chain in a crystallite is then described by the Hamiltonian given in Eqs. (1) and (2). It is the first term in Eq. (2) that provides the poling force; its coefficient A_1 may be written as

$$A_1 = \Delta - pE\,, \tag{7}$$

where 2Δ is a crystal-field splitting between the energy of a favorably aligned polymer unit in the field of its neighbors, and that of an unfavorably aligned unit, when there is no applied electric field. The last term in Eq. (7) is the dipole energy of the unit, with p the electric dipole moment in an electric field E.

The values of parameters in the Hamiltonian are shown in Table I. The angular frequency ω_0 of the undamped librational mode of zero wave number is given by the expression $\omega_0^2 = (|A_1| + 4A_2)/I$. Both ω_0 and the width λ of this spectral line are known from infrared spectroscopy,[8] while a and I

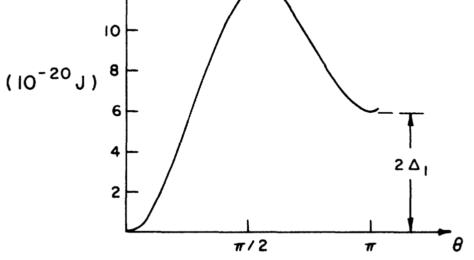

FIG. 1. Interchain contribution to the potential energy of a monomer unit of PVF_2 as a function of angle of rotation about its chain axis. The unit is located at the center of the orthorhombic unit cell of the β phase. All neighboring chains are aligned at $\theta = 0$.

TABLE I. Numerical values of quantities used in text.

ω_0	13.2 THz
λ	7.4 THz
I	1.305×10^{-45} kg m^2
p	7×10^{-30} cm
A_2	4.46×10^{-20} J
Δ_1	2.99×10^{-20} J
Δ_2	1.50×10^{-20} J
k	6.48×10^{-20} J
a	0.256 nm
v_0	1804 m sec^{-1}
$E_c^{(1)} = \Delta_1/p$	4.27 GV m^{-1}
$E_c^{(2)} = \Delta_2/p$	2.14 GV m^{-1}
N_{mono}(per chain)	40
A_6	2.43×10^{-21} J
A_{12}	1.30×10^{-20} J

are calculated directly from the crystal structure parameters.[9] The value of p is taken from Ref. 2. The interchain potential and k have been determined approximately from conformational analysis[10] through the molecular-structure-determination system CAMSEQ-II.[11] The atomic charge densities were computed from the semiempirical molecular-orbital scheme CNDO/2.[12] Our value for k fits the one which has also been calculated by Kobayashi *et al.*[8] We consider two values of Δ, corresponding to the case where all nearest-neighboring chains are aligned in the direction $\theta = 0$ $(\Delta = \Delta_1)$, and the case where three out of four nearest-neighboring chains are aligned in this direction, and one is oriented in the $\theta = \pi$ direction $(\Delta = \Delta_2)$. These values have been determined using conformational analysis, and allowing for a relaxation of neighboring chains. In a neutral environment Δ will vanish; such a situation might occur on the boundary between two oppositely oriented domains within a crystallite as illustrated in Fig. 2.

In order for it to be energetically favorable for a chain to reverse its dipole orientation from $\theta = 0$ to π, we must have $A_1 < 0$ in Eq. (2), and hence from Eq. (7) have $pE > \Delta$. This is equivalent to requiring E to exceed a critical value of Δ/p. Substitution of the appropriate numerical data from Table I shows that for a chain in a non-neutral environment this critical field must be of the order of 1 GV m^{-1}. Because this value is at least an order of magnitude greater than typical fields in which poling has been observed[1,13] we are led to restrict our attention to chains for which $\Delta = 0$, and which are thus expected to be found only in a domain wall as shown in Fig. 2.

When the potential defined in Eq. (2) is inserted in Eq. (4) one obtains a set of coupled nonlinear differential equations of motion which have not been solved analytically, even in the absence of the thermal-fluctuation term. There are, however, some known special solutions to the equation that is obtained by taking the continuum limit of Eq. (2) at zero temperature. That is, one replaces the difference $\theta_{i+1} - 2\theta_i + \theta_{i-1}$ by the differential $a^2\partial^2\theta/\partial x^2$, with a the repeat distance along the chain direction x, and ignores the thermal term $F(t)$. The equation that results,

$$I\ddot{\theta} = -A_1 \sin\theta - 2A_2 \sin 2\theta + ka^2(\partial^2\theta/\partial x^2) - \lambda I \dot{\theta}\,, \tag{8}$$

is known as the double sine-Gordon equation.[14,15]

Two trivial solutions to this equation are the constant values $\theta(x,t) = 0$ and π, which represent the system in a state of rest in either the absolute or subsidiary minimum of potential energy. More interesting are the "kink" solutions which describe the motion of the boundary between two regions of the chain, in one of which $\theta \simeq 0$ and in the other of which $\theta \simeq \pi$. In the present case the potential energy is lower for $\theta \simeq \pi$ and so this region advances at the expense of the region in which $\theta \simeq 0$. This is illustrated in Fig. 3. The form of this traveling solitary wave of electric polarization is

$$\theta(x,t) = 2\arctan\{\exp[2(x+vt)/d]\}\,. \tag{9}$$

Here v and d are, respectively, the velocity and width of the kink, and are given by

$$v = \frac{v_0}{(1 + 4A_2\lambda^2 I/A_1^2)^{1/2}} \tag{10}$$

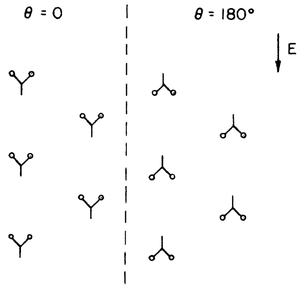

FIG. 2. At the boundary between oppositely polarized regions some chains are in a neutral environment for which the energies of either of two opposite orientations are approximately equal.

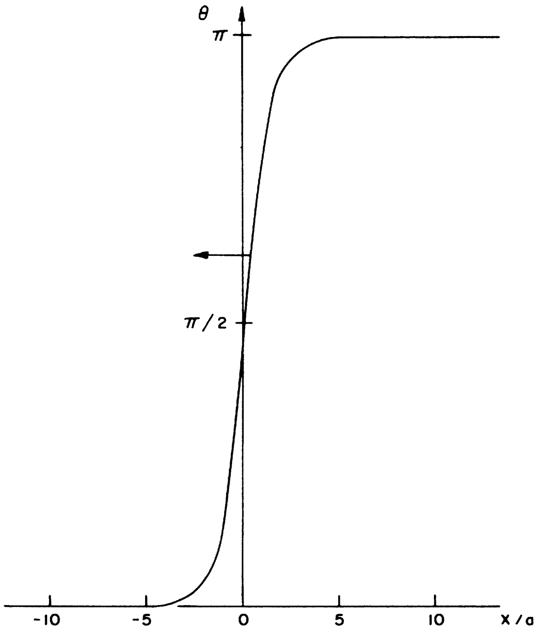

FIG. 3. Solution of the double sine-Gordon equation represents a kink traveling to the left.

and

$$d = 2I\lambda v / |A_1|, \tag{11}$$

with $v_0 \equiv (ka^2/I)^{1/2}$, the maximum velocity a kink assumes in an undamped chain.

The constant A_1 represents the effects of both the electric field E acting on a monomer of dipole moment p and also the short-range interchain potential. For a monomer in a position in which the short-range interactions favor equally the $\theta = 0$ and π positions the constant A_1 will be entirely due to the electric field, and we have $|A_1| = pE$. Then we find that Eq. (10) may be written in the form

$$v = v_0 E / [(E_0^2 + E^2)^{1/2}], \tag{12}$$

with $E_0 \equiv 2\lambda(A_2 I)^{1/2}/p$. Use of the data in Table I leads to the conclusion that $v_0 \simeq 1.8$ km sec^{-1} and $E_0 \simeq 16$ GV m^{-1}. Thus in a poling field of 100 MV m^{-1}, for example, the speed of propagation of the kink would be about 11 m sec^{-1}.

The electrical potential energy that is lost as the chain is poled is consumed by the damping term in Eq. (8), which is the phenomenological representation of the transport by phonons of kinetic energy to distant chains. The propagation speed v is governed by the balance between these two mechanisms.

III. NUMERICAL RESULTS

The approximation that yields the double sine-Gordon equation has a number of obvious weaknesses. One knows, for example, that the poling process is temperature dependent, and so the exclusion of the Brownian-motion term $F(t)$ from Eq. (4) allows only a zero-temperature result to be predicted. One must also expect the discrete nature of the polymer chain to play a significant role in the motion of a kink of polarization. From Eq. (11) one finds the predicted width d of a kink to be about 0.3 nm, and thus roughly equal to the repeat length along the chain, clearly invalidating the continuum approximation.

In view of these inadequacies of the analytical approach, a series of computer experiments were performed in which the discrete nature of the chain and the thermal fluctuations were taken into account. A chain of 40 monomer units was chosen for study, in accord with experimental observations of lamellar thickness.[1] The equations of motion, Eqs. (4), were solved by linearization and direct integration over a small time increment Δt. The thermal forces defined in Eqs. (5) and (6) were included by adding an impulse of fixed magnitude $(2\lambda I k_B T/\Delta t)^{1/2}$ but of random sign during each time increment. Because of the random nature of the force all the finite-temperature experiments were performed repeatedly and average values taken. The error bars in the graphs below indicate the statistical spread of the results.

Some results of these computations are shown in Fig. 4, in which the speed of propagation v of a 180° kink is shown for various temperatures as a function of electric field. At zero temperature the discrete nature of the chain makes its presence felt in the form of a critical field E_c, below which no motion of the kink can occur. At finite temperatures v is proportional to E for small fields with a coefficient that varies exponentially with inverse temperature, as is to be expected in a process that is an analog of hopping conductivity in semiconductors. At very large fields ($E \gg E_c$) the speed becomes independent of temperature and equal to the prediction of the continuum theory. At the typical poling temperature of 373 K and at a field of 200 MV m^{-1} the speed is about 9 m sec^{-1}.

Having established that a kink may be expected to propagate fairly rapidly through the lamellar width, we must now consider the more difficult question of the creation of kinks. The most probable location for a kink to originate is at the point where a chain emerges from the crystallite and enters the amorphous region; because kinks can only be created in pairs in the body of the crystallite, twice as much energy would then be required.

The forces acting on a chain at the crystallite boundary are to some extent an unknown quantity. The absence of crystalline order in the amorphous region may well provide an opportunity for a kink to form at only a small cost in energy; on the other hand, the very existence of the boundary suggests the presence of torsional forces resisting

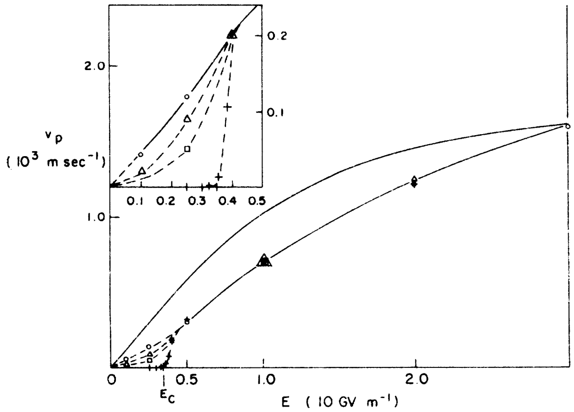

FIG. 4. Propagation speed v of a 180° kink in a finite discrete chain is plotted as a function of electric field E for various temperatures; + = 0 K, □ = 187.5 K, △ = 373 K, ○ = 750 K. The uppermost line is the analytic result for the continuum approximation at $T = 0$.

further growth of the crystal surfaces, and these forces might be inimical to kink formation. In the absence of clear knowledge of this environment we make the simplest neutral assumption and suppose the chain simply to terminate at the lamellar boundary with no external intrachain forces present. With this assumption we can then perform a computer experiment to determine the waiting time t_w that on average elapses between application of the field E and passage of a kink into the crystallite along a given chain. The results of this study are shown in Fig. 5, in which $\ln t_w$ is plotted as a function of inverse temperature for various fields. These results show t_w to be considerably larger than the transit times of a kink across a lamella. From Fig. 4, for example, we see that the 10-nm width of a lamella would be traversed in about 20 psec at 373 K in a field of 10 GV m^{-1}, whereas t_w is about 70 nsec under similar conditions. We thus interpret Fig. 5 by assuming the propagation of the kink to occupy a negligible time in comparison with that necessary for the appropriate energy fluctuation to occur to create a kink. The approximately linear behavior suggests that a picture of thermally activated kink creation is valid, with

$$t_w = Ae^{B/T}. \tag{13}$$

The "attempt frequency" A^{-1}, found from the common extrapolations of the lines to infinite temperature, yields a value of about 7 THz, which is to be compared with the figure of 8.4 THz obtained by multiplying twice the librational frequency at zero wave number of 2.1 THz by a further factor of 2 to allow for the two ends of the chain. The activation energy Bk_B, found from the slope of these lines, can be interpreted satisfactorily in terms of the contributions of the various terms in the Hamiltonian given in Eqs. (1) and (2).

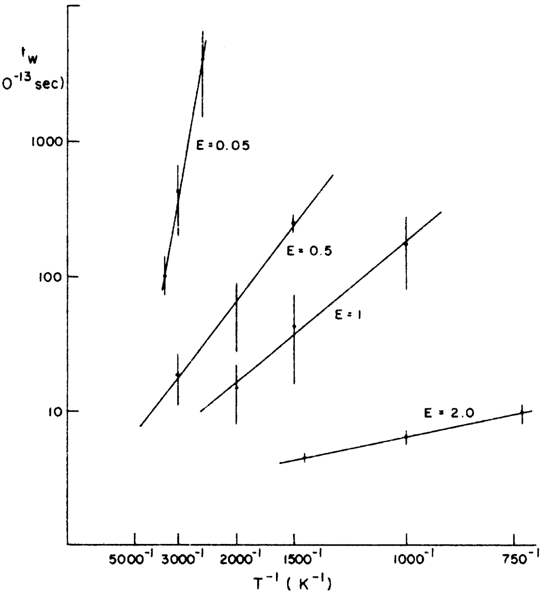

FIG. 5. Logarithm of the average waiting time t_w for creation of a 180° kink is shown as a function of T^{-1} for various fields E in units of 10 GV m^{-1}.

The average waiting time for a chain to reverse its electric polarization under typical poling conditions ($T = 373$ K, 500 MV m^{-1}) and in a neutral crystal environment is predicted by this model to be of the order of 7×10^4 sec. The theoretical poling time for the entire sample will clearly be much larger than this, in disagreement with the experimentally observed poling times.[13] This indicates some inadequacy either of the model as a whole or of the assumed nature of the crystallite amorphous boundary.

IV. THE 60° MODEL

In calculating the interchain potential energy of a chain in a particular orientation the question naturally arises of how many neighbors need be taken into account. Because the structure of the β phase is orthorhombic it is tempting to include only the four nearest-neighboring chains. This, however, would be inaccurate because the two next-nearest-neighboring chains are located at a distance only 0.1 percent further away than the nearest ones,[9] and the structure is, in fact, close to being equilateral triangular or centered hexagonal.

The closeness of the structure to a hexagonal form led Kepler and Anderson[1] to make an ingenious suggestion of an alternative mechanism of poling, namely that a rotation of the chains through 60° rather than 180° plus a small distortion of the lattice might be the correct model. This possibility is illustrated in Fig. 6, in which the boundary

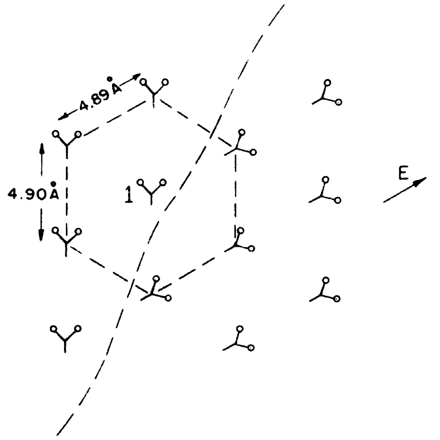

FIG. 6. Boundary between regions of β-phase PVF$_2$ differing in direction of polarization by 60°.

between such twinned regions is shown. Some support for such a mechanism has recently been given in the form of infrared studies in which the optical properties of a PVF_2 surface were shown to be modified by poling.[16] A simple reversal of chain orientation through 180° would presumably have left these unchanged.

The first step in studying this model was the calculation of the interchain potential of the chain labeled 1 in Fig. 6, for which by symmetry the potential for $\theta = 0$ is approximately equal to that for $\theta = 60°$. The result of this computation, which again was performed using the methods of conformational analysis,[10] is shown in Fig. 7. The striking aspect of this potential is the subsidiary minimum that occurs at $\theta = 30°$, which shows that a partial rotation of the chain between the polarizations of the two parts of the twinned crystal can be metastable. This complicates the analysis to some degree, and renders the double sine-Gordon equation an inadequate description of the model. It was thus necessary again to turn to a computer experiment to determine the behavior of this model in a poling electric field. The interchain potential was modeled by replacing Eq. (2) with the expression

$$U = \sum_i \left[A_6(1-\cos 6\theta_i) + A_{12}(1-\cos 12\theta_i) - pE\cos(\pi/3-\theta_i) + \tfrac{1}{2}k(\theta_i-\theta_{i+1})^2\right], \quad \theta \leq \theta_i \leq \pi/3. \tag{14}$$

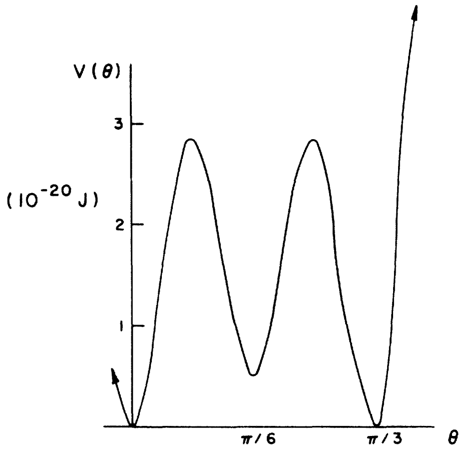

FIG. 7. Potential energy as a function of rotational angle θ for the chain at the center of the dashed hexagon in Fig. 6. The zero of θ is the vertical direction.

The constants A_6 and A_{12} chosen as the best fit to the calculated potential are given in Table I. The direction of the field E is shown in Fig. 6.

The results of the computation indicate that the 30° minimum in Fig. 7 has a marked effect in facilitating the formation of kinks. In the 180° model no kink-antikink pairs were formed at normal temperatures near the middle of the chain because of the double energy required. In the 60° model, however, the intermediate minimum in the potential appears to trap segments of the chain with comparative ease, which then separate and complete the transition to 60° independently. A typical conformation is shown in Fig. 8, which was generated from a chain at rest at $\theta = 0$ after 0.4 psec at 373 K in a field of 20 $GV\,m^{-1}$.

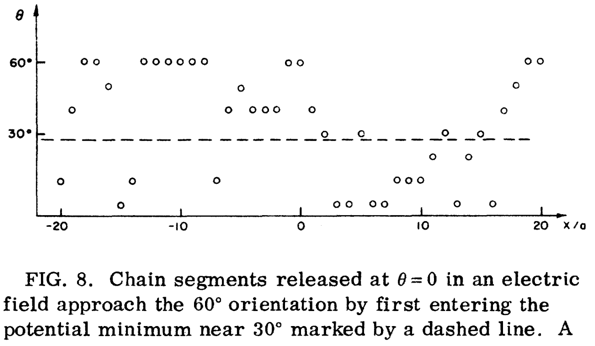

FIG. 8. Chain segments released at $\theta = 0$ in an electric field approach the 60° orientation by first entering the potential minimum near 30° marked by a dashed line. A typical set of rotational angles along a chain is shown at 0.4 psec in a field of 20 $GV\,m^{-1}$ at 373 K.

A summary of the computations on this model is shown in Fig. 9, in which t_p^{-1}, the reciprocal of the total overturning time of a single chain is shown as a function of electric field and temperature. A limitation of the direct computational approach is seen when one notes that the regime covered is one in which exceedingly large fields (of the order of 10 $GV\,m^{-1}$) are present, with con-

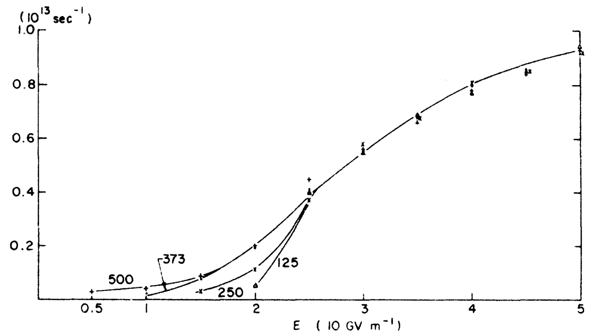

FIG. 9. Total overturning time (per chain) t_p is plotted for the 60°-rotation model as a function of electric field for various temperatures.

sequent overturning times of the order of psec. Because the motion of the chain takes place in a time scale of the order of the librational period of about 0.1 psec, the time increment used in the computations must be much less than this and was typically 1 fsec. It is thus not possible to follow the motion for times much longer than a few tens of psec within reasonable computational limits. In order to obtain an estimate of the behavior at more modest electric fields it was decided to extrapolate the high-field results, and to this end the semilogarithmic graph shown in Fig. 10 was plotted. The straight lines are again the result of the thermal activation process. If these lines are then continued down to fields of the order of 100 $\mathrm{MV\,m^{-1}}$, then at a temperature of 373 K an overturning time of the order of 50 psec is predicted. The validity of this extrapolation depends on the criterion $npE > k_B T$, with n the number of monomer dipoles constituting the average kink-free segment of chain. This criterion should be satisfied down to fields of the order of 20 $\mathrm{MV\,m^{-1}}$ at 373 K.

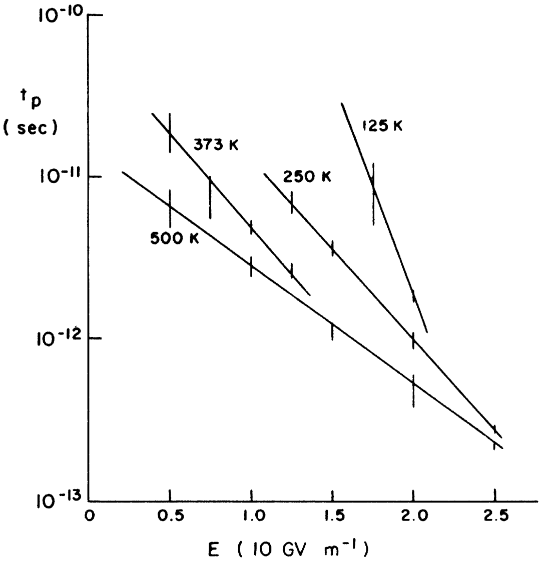

FIG. 10. This plot is used to estimate by extrapolation the value t_p might have under typical poling conditions.

Because only a chain in a neutral crystal environment is free to rotate in modest fields, there will only be very few chains in a crystallite at any time that can participate in the poling process. Such chains will be at the boundary surface between differently polarized sections of the crystallite as shown in Fig. 6 and will also be on the line of advancing polarization in that surface. The poling process will thus proceed in a more or less sequential way, one chain at a time. This allows us to estimate a poling time for the sample as a whole by merely multiplying t_p by the number of chains in a crystallite, which may typically be of the order of 10^7. The poling time produced in this way is of the order of 1 msec.

V. CONCLUSION

We have examined the poling process in β-phase $\mathrm{PVF_2}$ in terms of propagation of a kink of rotation along the length of a chain and through the width of a lamella. In the first model studied this kink represented a rotation of 180°. The calculation led to a prediction of extremely long waiting times before such a kink could be activated at normal temperatures, and thus did not provide good accord with the observed poling times for real samples which are apparently of the order of a few seconds.[13] In the second model studied a rotation of 60° was considered and in this case rather rapid poling times of the order of 1 msec were predicted.

While neither theory provided immediate agreement with experiment, one must remember that both were based on highly idealized models and thus are likely to provide only lower bounds to the actual poling times. The existence of head-to-head defects in the chain of the form $\mathrm{CH_2{-}CF_2{-}CF_2{-}CH_2}$ would certainly impede the progress of a propagating kink and slow the poling process. It is also likely that the small change in crystal axis dimension that occurs in the 60°-rotation model would cause internal strains in the crystallite that would impede the transition.

Our conclusion is that we have been unable to reconcile with experiment a model in which chain rotations through 180° occur as part of the poling process. A model involving rotations through 60°, on the other hand, appears to give results not inconsistent with observed poling times.

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[1] See, for example, R. G. Kepler and R. A. Anderson, J. Appl. Phys. 49, 4490 (1978).

[2] Y. Wada and R. Hayakawa, Jpn. J. Appl. Phys. 15, 2041 (1976).

[3] See, for example, D. Naegele and D. Y. Yoon, Bull. Am. Phys. Soc. 23, 379 (1978).

[4] E. W. Aslaksen, J. Chem. Phys. 57, 2358 (1972).

[5] A. J. Hopfinger, A. J. Lewanski, T. J. Sluckin, and P. L. Taylor, in *Solitons and Condensed-Matter Physics*, edited by A. R. Bishop and T. Schneider (Springer, New York, 1979).

[6] N. C. Banik, F. P. Boyle, T. J. Sluckin, P. L. Taylor, S. K. Tripathy, and A. J. Hopfinger, Phys. Rev. Lett. 43, 456 (1979).

[7] H. A. Kramers, Phys. Fenn. 7, 284 (1940).

[8] M. Kobayashi, K. Tashiro, and H. Tadokoro, Macromolecules 8, 158 (1975).

[9] J. B. Lando, H. G. Olf, and A. Peterlin, J. Polym. Sci. A4, 941 (1966).

[10] A. J. Hopfinger, *Conformational Properties of Macromolecules* (Academic, New York, 1973).

[11] R. Potenzone, Jr., E. Cavicchi, H. J. R. Weintraub, and A. J. Hopfinger, Comput. Chem. 1, 187 (1977).

[12] J. A. Pople and D. C. Beveridge, *Approximate Molecular Orbital Theory* (McGraw-Hill, New York, 1970).

[13] J. E. McKinney, G. T. Davis, and M. G. Broadhurst, J. Appl. Phys. 51, 1676 (1980).

[14] S. Duckworth, R. K. Bullough, P. J. Caudrey, and J. D. Gibbon, Phys. Lett. 57A, 19 (1976).

[15] J. D. Gibbon, N. C. Freeman, and R. S. Johnson, Phys. Lett. 65A, 380 (1978).

[16] D. Naegele and D. Y. Yoon, Appl. Phys. Lett. 33, 132 (1978).