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Cooperative Chain Rotations as a Mechanism of the α–δ Phase Transition in Poly(vinylidene fluoride)

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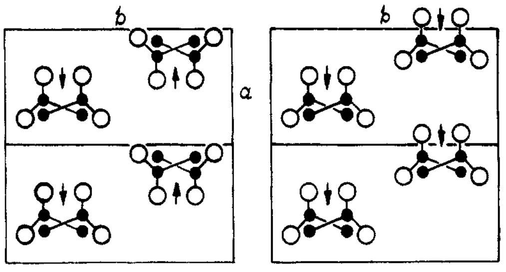
ABSTRACT: Possible microscopic mechanisms of the electric-field-induced transition from the nonpolar α-phase to the polar δ-phase in poly(vinylidene fluoride) are analyzed theoretically. The energetics characterizing the mechanism connected with independent chain rotations is calculated. It is shown that this mechanism becomes energetically favorable only in the range of very high electric fields $E > E_{cr}$, within which the α-phase transforms into the β-phase, but not into the δ-phase. Owing to this result we propose another transition mechanism, which involves cooperative rotations of neighboring chains in polymer crystallites. It is emphasized that two-dimensional correlations of chain rotations should play the main role in the α–δ-phase transition. The activation energy characterizing the formation of "two-dimensional" δ-phase nuclei is derived and evaluated. The kinetics of the α–δ-phase transition is calculated in the frame of the theory of absolute reaction rates. A characteristic time τ of this structural transformation is estimated and compared with available experimental data.

I. Introduction

Poly(vinylidene fluoride) (PVDF) and related copolymers are marked for ferroelectric properties, which are displayed by certain crystal forms of these polymers.[1,2] This feature is due, in particular, to large electric dipole moments normal to the chain axis that are carried by VDF-containing macromolecules. However, under usual conditions PVDF crystallizes in the nonpolar α-phase. In this case transverse dipole moments of two neighboring chain segments, which form the unit cell, have antiparallel orientations and so compensate each other. Subsequent mechanical orientation of the α-PVDF at temperatures below 90 °C yields the ferroelectric β-phase.[3] The observed phase transition involves a change in chain conformation from *trans–gauche–trans–gauche′* to the *all-trans* conformation. On the other hand, the drawing at higher temperatures is not accompanied by a phase transformation so that in this case oriented films containing predominantly the α-phase are produced.[1] When electric fields of the order 100–150 MV/m are applied to these films, a transition from the α-phase to the highly polar δ-phase takes place.[4–6] It should be emphasized that δ-PVDF displays piezoelectric and pyroelectric coefficients of the same order as those obtained for poled β-PVDF films.[1,6]

The α–δ-phase transition is the only structural transformation in PVDF which leaves the chain conformations unchanged.[1] This feature lends increasing importance to experimental and theoretical studies of a microscopic mechanism of this transition. The X-ray diffraction data[4] indicate that the unit cells in the α- and δ-crystal forms have essentially the same dimensions. These data and infrared results enabled Naegele et al.[4] to conclude that the α–δ transformation proceeds via the 180° rotation of every second molecular chain in the unit cell of the α-form such that the antiparallel dipolar alignment in the unit cell is changed to the parallel alignment due to the applied electric field (see Figure 1). Further X-ray analysis[6] has shown that this rotation is accompanied by a chain translation along its axis of about one-quarter of the lattice period c.



a) b)

Figure 1. Crystal structures of the nonpolar α-form (a) and of the polar δ-form (b) of PVDF. The projection onto the ab plane perpendicular to the polymer chains is shown. a and b denote the dimensions of the unit cell. Large and small circles represent fluorine and hydrogen atoms, respectively. Arrows indicate net dipole moments normal to the chain axis.

Obviously, it is necessary to overcome certain potential barriers in order to realize molecular reorientations leading to the α–δ transformation. Therefore, a theoretical problem arises which consists of the elucidation of a particular mechanism of molecular motions enabling the minimization of the height of potential barriers hindering the formation of the δ-phase. Dvey-Aharom, Taylor, and Hopfinger[7] attempted to solve this problem already in 1980; they proposed a transition mechanism involving independent reorientations of individual macromolecules. In the present work we reconsider this mechanism and demonstrate that it cannot be realized in the range of applied electric fields, within which the α–δ transformation can be observed (see section II). Owing to this result we propose another transition mechanism, which consists of a *cooperative* rotational–translational motion of neighboring chains in polymer crystallites. Then, we evaluate an activation energy of the δ-phase nucleation that characterizes this mechanism (section III). Finally, we calculate the kinetics of the field-induced α–δ-phase transition in PVDF (section IV).

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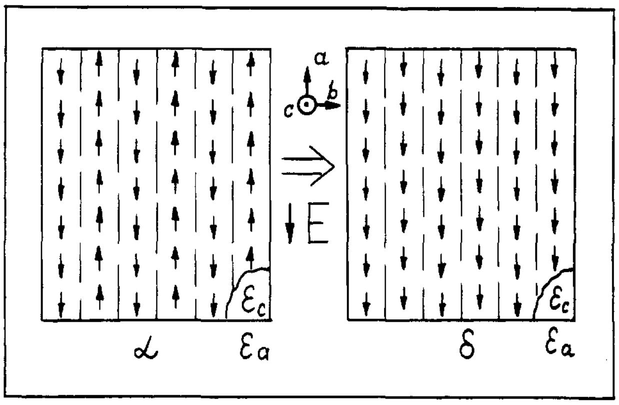

Figure 2. Reorientation of molecular electric dipoles at the α–δ-phase transition. The cross-section of a polymer crystallite being perpendicular to the polymer chains is shown. Dashed lines designate the boundaries of monomolecular layers. ϵ_a and ϵ_c are the electric permittivities of the amorphous and crystal phases, respectively.

II. Analysis of the Transition Mechanism Connected with Independent Chain Reorientations

An important feature of the α–δ-phase transition is that only half of the chains participate in a rotational–translational motion (R–T motion) resulting in the structural transformation. Moreover, these reorienting chains form monomolecular layers parallel to the crystallographic *ac* plane (see Figure 2), which are separated by monolayers of chains retaining their original orientation. Since the unit cell dimensions and the chain conformations do not change during the structural transformation, the intramolecular energies and the energies of interactions between macromolecules within each monolayer should be the same in the α- and δ-crystal phases.

According to theoretical estimates,[8] the total free energy of the δ-phase is higher than that of the α-phase in the whole temperature range studied. This energy difference can be attributed to changes in the packing energy of adjacent monomolecular layers and in the energy of dipole–dipole interactions. Therefore, the α–δ transformation becomes thermodynamically feasible only in external electric fields exceeding a certain threshold field E^*. For an infinite crystal lattice, this threshold field can be written as

$$E^* = \gamma_b c/2p \tag{1}$$

where $p = (p_\alpha + p_\delta)/2$, p_α and p_δ are the transverse dipole moments of individual *tgtg′* units in the α- and δ-phases respectively, and γ_b is the excess energy per unit length of a reoriented chain in the δ-phase, which includes a contribution arising from the short-range interactions between this chain and its nearest neighbors located in two adjacent layers and a contribution from the long-range dipole–dipole interactions with all the chains located in the layers not involved in R–T motions. In deriving eq 1, we have taken into account the work done by the applied electric field E during the 180° reorientations of molecular dipoles at the phase transition. The correcting term proportional to the derivative $\mathrm{d}p/\mathrm{d}E$ was omitted since our estimates have shown that the contribution of a non-zero polarizability of the PVDF molecules, which causes this term, is small in comparison with the above work.

Let us ascertain now the physical conditions under which the transition mechanism[7] connected with independent chain reorientations can operate. Firstly, we calculate a minimum applied field E_{cr} that makes energetically favorable the reorientation of a first chain inside the α-form crystallite. The increase ΔW_1 in the energy of this crystallite due to the formation of a "one-dimensional" δ-phase nucleus, having only one unit cell in each cross-section, can be represented as

$$\Delta W_1 = (\gamma_b + 2\gamma_a + \Delta u_1)L_c \tag{2}$$

where $2\gamma_a$ is the increase in the energy of short-range interactions of the rotated chain and its two nearest neighbors in the *ac* crystal plane, Δu_1 is the change in the energy of dipole–dipole interactions between this chain and all other chains that have to be reoriented in order to form the δ-form crystallite (γ_a and Δu_1 are calculated per unit length of a chain), and L_c is the thickness of a crystallite measured along the chain axes. By definition, the critical field E_{cr} can be calculated as an electric field producing work during 180° rotations of molecular dipoles, which exactly compensates for the energy increase ΔW_1 due to the formation of a one-dimensional nucleus. Accordingly, from eq 2 we obtain

$$E_{cr} = \frac{(\gamma_b + 2\gamma_a + \Delta u_1)c}{2p} = E^* + \frac{\gamma_a c}{p} + \frac{\Delta u_1 c}{2p} \tag{3}$$

To proceed further, we have to estimate the numerical values of the energies involved in eq 3. The rigorous calculation of the electrostatic energy Δu_1 calls for the solution of a system of N simultaneous equations because the polarizability of the PVDF molecules cannot be ignored here. The number N of molecular dipoles in a crystallite, which differ in electric moment owing to different internal fields acting on them, is very large (especially in the case of a three-dimensional spatial distribution of an internal electric field considered in the next section). Therefore, the rigorous calculation of the depolarization energy appears to be extremely difficult. On the other hand, the electrostatic energy Δu_1 can be evaluated in the first approximation, if we replace the actual discrete arrangement of molecular dipoles in a crystallite by a distribution of infinitesimal dipole moments with the densities of $\pm 2p/abc$. In this continuum approximation the source of the depolarization field created by a one-dimensional δ-phase nucleus can be represented by a pair of oppositely charged stripes having the length L_c and the width $b/2$. These stripes are separated by one lattice period along the crystallographic axis *a*; the densities of effective polarization charges distributed along their surfaces have the magnitude $\sigma = 4p/abc$. Regarding the crystal phase as an isotropic dielectric medium with an appropriate relative permittivity ϵ_c (the dielectric anisotropy in PVDF crystallites is very weak[9]) and using elementary electrostatics, it is possible to derive the following approximate expression for the depolarization energy of a one-dimensional nucleus

$$\Delta u_1 = \frac{p^2}{\pi \epsilon_0 \epsilon_c a^2 c^2} \times \left(\ln\frac{4a^2 + b^2}{b^2} - 4\frac{a^2}{b^2} \ln\frac{4a^2 + b^2}{4a^2} + 8\frac{a}{b} \arctan\frac{b}{2a} \right) \tag{4}$$

where ϵ_0 is the permittivity constant, and we have taken into account that the length L_c of this nucleus is much larger than its transverse dimensions *a* and *b*. It should be emphasized that the dielectric constant ϵ_c appearing in eq 4 allows for the non-zero polarizability of the PVDF molecules. (These two quantities are known to be connected by the Clausius–Mossotti relation.) We note also that the depolarization energy (4) tends toward infinity

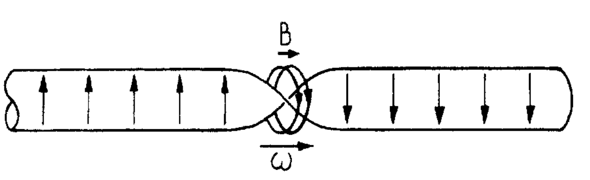

Figure 3. Chain defect being an elementary carrier of dipolar reorientations at the α–δ transformation. The combination of dislocation and disclination loops, which model this defect, is shown. $\vec{\omega}$ is the Frank vector of a disclination loop and $\vec{B}$ is the Burgers vector of a dislocation loop.

in the limit of small b if the dipole moment p is kept constant. However, in this imaginary case the density of polarization charges $\sigma = 4p/abc$ also tends toward infinity, thus causing an infinite depolarization energy. If, instead of the dipole moment p, the density σ is kept constant, the depolarization energy will tend toward zero in the limit of small b, in agreement with that expected from general physical reasons. Substituting into eq 4 numerical values of the involved physical quantities, i.e. $a = 4.96$ Å, $b = 9.64$ Å, $c = 4.62$ Å, $p \approx 8 \times 10^{-30}$ C m,[1] and $\epsilon_c \approx 6$,[10-12] we find that the contribution to the critical field E_{cr}, which is due to the last term in eq 3, equals approximately 700 MV/m.

The order-of-magnitude estimation of the excess packing energy γ_a can be made on the basis of our former paper,[13] where excess energies of similar origin were evaluated for β-PVDF. This gives $\gamma_a \sim 10^{-11}$ J/m. Accordingly, the second term in eq 3 is expected to be of the order of 600 MV/m. In the total, the critical field E_{cr} can be estimated as $E_{cr} \approx E^* + 1300$ MV/m. It is important that E_{cr} appears to be considerably higher than the applied field $E \sim 500$ MV/m, which was shown[5] to induce the transformation of the α-phase into the β-phase, in contrast to the fields $E \sim 100$–150 MV/m inducing the α–δ-phase transition.

Thus, the independent R–T motions of individual chains cannot be energetically favorable in the range of applied fields, within which the α–δ transformation can take place. This statement should be valid even for the chains immediately adjacent to the crystallite faces perpendicular to the a axis since the energy increase ΔW_1 characterizing reorientations of these chains is estimated to be only about 2 times smaller than that calculated above for the inner chains. The antiphase domain boundaries, which were predicted to exist in the α-phase,[14,15] also cannot promote independent chain reorientations since in the dominant orientation they are parallel to the "polar" axis a.

Independent R–T motions of *very short chain segments*, of course, can occur with the aid of thermal fluctuations even in applied fields much lower than E_{cr}. In this case at the ends of reoriented segments the zones of elastic twisting and stretching or contraction of a chain are formed. (Within these zones only small changes in the torsional and valence angles and slight deformations of skeletal bonds should take place.) Each zone can be regarded as a defect of a macromolecule being equivalent to the twist disclination loop[16,17] of strength 180° combined with the prismatic dislocation loop[17] having the Burgers vector $B \approx c/4$ (Figure 3). The formation of such a defect at a crystallite face normal to the chain axes and its subsequent motion along the chain up to the opposite face would produce the reorientation of this chain necessary for the δ-phase nucleation, as was proposed in ref 7. However, during this motion a restoring force will act on a defect since the lengthening of the reoriented segment will be accompanied by an increase in the crystallite energy given by an expression similar to (2). It can be shown that the counteraction of this restoring force can be overcome only by the driving force of an external field exceeding the critical field E_{cr} defined again by eq 3.

Thus, we may conclude that the mechanism of independent reorientations of individual macromolecules cannot ensure the observed α–δ-phase transition in PVDF.

III. Energetics of Cooperative Chain Reorientations in α-PVDF

Theoretical considerations reported in the previous section indicate that the α–δ transformation should occur via cooperative R–T motions of macromolecules. Since the α-phase has a laminated structure, the main role in this transformation must be two-dimensional correlations of chain rotations within individual monomolecular layers.

The most simple version of cooperative R–T motion consists of the simultaneous reorientation of all molecular dipoles in a single monolayer that is realized by changing the setting angles θ of chains in the unit cells from the initial value θ_0 to the final one $\theta_0 + 180°$. However, the minimum applied field E^{**}, which enables us to surmount the potential barrier hindering such a simultaneous reorientation without the aid of thermal agitation, is expected to be of the order of the critical field E_{cr} given by eq 3, i.e. $E^{**} \sim 1000$ MV/m. At the same time this barrier, being proportional to the layer area, is evidently too high to be surmounted with the aid of thermal fluctuations in much lower fields $E \sim 100$ MV/m. Accordingly, the mechanism involving simultaneous reorientation of the whole monolayer cannot be realized in the range of applied fields, within which the α–δ transformation can take place.

Proceeding from the above discussion, we postulate that the dominant mechanism of the α–δ-phase transition consists of the thermally activated formation of "two-dimensional" δ-phase nuclei, which include relatively short segments of several neighboring chains, and their subsequent growth due to the motion of phase boundaries within monomolecular layers. This mechanism minimizes the contribution to the potential barrier of chain reorientations due to an increase in the packing energy of chain segments acquiring intermediate setting angles θ_i between θ_0 and $\theta_0 + 180°$ during their R–T motion. If the critical dimensions of the δ-phase nucleus, corresponding to a saddle point of the total potential barrier, are much larger than the unit cell dimensions, then the contribution provided by excess packing energies of short chain segments having *temporarily* such intermediate setting angles θ_i can be neglected in comparison with the main contribution given by the energy of a phase boundary enveloping this nucleus.

Let us study in a continuum approximation the energetics characterizing the formation of a two-dimensional δ-phase nucleus. For simplicity, we consider the nucleus of a rectangular shape (Figure 4). The boundaries of this nucleus that are perpendicular to the crystallographic c axis carry linear arrays of twist disclination loops combined with prismatic dislocation loops, each loop enveloping a single chain. Since these defects create only short-range strain fields,[18] the self-energy of such a boundary should be proportional to its length h in a good approximation and so can be defined by introducing an energy γ_c per unit length. (We assume that the critical dimensions l^* and h^* of a nucleus, which are calculated below, satisfy the inequalities $h^* \gg a$ and $l^* \gg c$.) In turn, the boundaries parallel to the c axis carry effective polarization charges distributed with a linear density $q = 2p/ac$. The depolarization energy ΔU of a nucleus having these charged boundaries can be calculated with the aid of a procedure

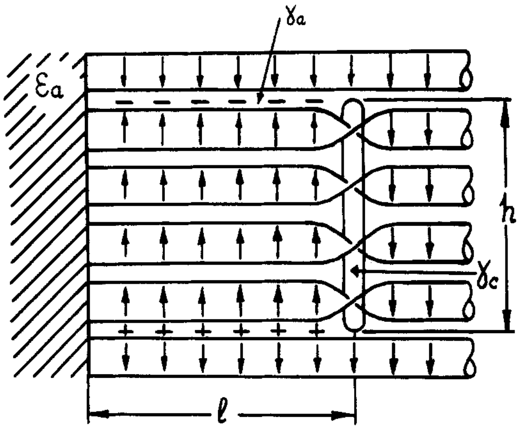

Figure 4. Schematic illustration of a two-dimensional δ-phase nucleus formed at the crystallite face contacting the amorphous phase.

similar to the one used to evaluate the electrostatic energy Δu_1 in section II. The calculation yields

$$\Delta U = \frac{p^2 l}{\pi a^2 c^2 \epsilon_0 \epsilon_c}\left(\ln \frac{16 l^2 (r - l)}{b^2 (r + 1)} + \frac{2r}{l} - \frac{2h}{l} + 1\right) \qquad (5)$$

where h and l are the nucleus dimensions along the axes a and c, respectively, and $r^2 = h^2 + l^2$.

The change $\Delta\Phi$ in the Gibbs free energy of the polymer crystallite due to the formation of a single two-dimensional δ-phase nucleus can be represented by the following sum:

$$\Delta\Phi = 2\gamma_a l + \gamma_c h + \gamma_b \frac{lh}{a} + \Delta U(l,h) - 2pE\frac{lh}{ac} \qquad (6)$$

where the first three terms account for the self-energy of the formed phase boundary and for the excess free energy of the δ-phase (see section II), ΔU is the depolarization energy given by (5), and the last term in (6) is the work done by the external electric field E during the reorientation of molecular dipoles within the nucleus. When deriving eq 6, we have assumed that the nucleation takes place near one of the crystallite faces perpendicular to the chain axes (see discussion in the next section). In this case the second term in (6) is only half of its normal value.

Substituting eq 5 into eq 6, we can obtain $\Delta\Phi$ as a function of the dimensions l and h of a nucleus explicitly. The critical dimensions l^* and h^*, corresponding to a saddle point of the function $\Delta\Phi(l,h)$, can be found from the following system of equations:

$$\left.\frac{\partial \Delta\Phi(l,h)}{\partial l}\right|_{l=l^*} = 0 \qquad \left.\frac{\partial \Delta\Phi(l,h)}{\partial h}\right|_{h=h^*} = 0 \qquad (7)$$

In turn, l^* and h^* define the height of the potential barrier $\Delta\Phi^* = \Delta\Phi(l^*,h^*)$ that has to be overcome in the process of formation of a δ-phase nucleus.

It is not possible to derive an analytic expression for the barrier height $\Delta\Phi^*$ and to find the dependence of $\Delta\Phi^*$ on the intensity E of an applied field explicitly since the logarithmic function is involved in eq 5, which defines the depolarization energy ΔU. Nevertheless, we can demonstrate the general trend of this field dependence with the aid of the following approximate calculation. We introduce a linear approximation $\Delta U = \Delta u l$ for the depolarization energy, thus neglecting the relatively weak dependence of the expression in brackets involved in eq 5 on the nucleus dimensions l and h. In this approximation the critical dimensions l^* and h^* calculated from eqs 6 and 7 can be written as

$$l^* \approx \frac{\gamma_c ac}{2p(E - E^*)} \qquad h^* \approx \frac{(2\gamma_a + \Delta u)ac}{2p(E - E^*)} \qquad (8)$$

where the energy γ_b is replaced by the threshold field E^* in accordance with eq 1. Using eqs 6 and 8, we find the barrier height as

$$\Delta\Phi^* \approx \frac{(2\gamma_a + \Delta u)\gamma_c ac}{2p(E - E^*)} \qquad (9)$$

where $\Delta u = \Delta U/l$ should be derived from eq (5) at $l = l^*$ and $h = h^*$ and so relatively weakly depends on the field intensity E.

Equation 9 demonstrates that the function $\Delta\Phi(l,h)$ really has a saddle point. Therefore, the thermally activated formation of nuclei with dimensions $l > l^*$ and $h > h^*$ will be followed by their spontaneous expansion, leading to the appearance of stable δ-phase layers. Equation 9 also shows that the barrier height $\Delta\Phi^*$ gradually decreases with increasing intensity E of the applied field.

In order to evaluate the barrier height quantitatively we have performed numerical computations of $\Delta\Phi(l^*,h^*)$ with the aid of eqs 5–7. In these computations we assumed the energy γ_c to have the value 2×10^{-11} J/m, which was found from ref 7 where the energetics of chain twisting in α-PVDF was calculated. We also used the values of other material parameters given in section II. The excess energy γ_b of the δ-phase was taken to be $\gamma_b = 1.8 \times 10^{-12}$ J/m at room temperature in accordance with the recent detailed energetic calculations.[9] With this value eq 1 gives the threshold field $E^* = 50$ MV/m, which is lower than the theoretical estimate of $E^* = 140$ MV/m obtained earlier in ref 8. This discrepancy may be explained by the fact that the calculations performed by Banik et al.[8] seem to overestimate E^* considerably since the chain translations during the α–δ transformation were set equal to $c/2$, but not to $c/4$ as suggested by X-ray measurements.[6]

The results of our numerical calculations are shown in Figure 5. It can be seen that the field dependence of the barrier height $\Delta\Phi^*$ deviates comparatively slightly from the law predicted by eq 9. For a typical applied field of $E = 150$ MV/m, the critical dimensions of the δ-phase nucleus are equal to $l^* \approx 28$ Å and $h^* \approx 105$ Å, and the barrier height $\Delta\Phi^*$, which can be also termed an activation energy of the formation of two-dimensional δ-phase nuclei, amounts to $\Delta\Phi^* = 42kT$ (k is the Boltzmann constant and T is the absolute temperature). This result indicates that the two-dimensional δ-phase nucleation should have an appreciable probability (see section IV).

IV. Kinetics of the α–δ Phase Transition

According to our theory, the kinetics of the α–δ transformation is defined by the process involving random δ-phase nucleation in different monolayers of various crystallites and subsequent growth of two-dimensional nuclei within each of these layers. It is supposed that the formation of δ-phase nuclei occurs more often near the crystallite faces normal to the chains (see Figure 4). In this case molecular defects, which are formed at the nucleus boundary immediately adjacent to the crystallite face, diffuse into the amorphous phase so that the energy of this boundary becomes negligible and the barrier height $\Delta\Phi^*$, according to eq 9, appears to be 2 times lower than the one characterizing the nucleation inside the crystallites. At the same time the number of nucleation sites at these faces is by a factor of $L_a/L_c \gg 1$ larger than the number of nucleation sites at the crystallite faces perpendicular

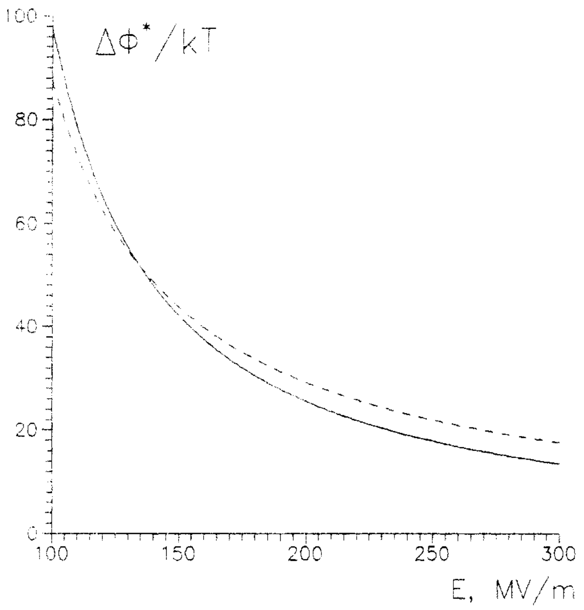

Figure 5. Height $\Delta\Phi^*$ of the potential barrier, which has to be surmounted during the formation of a two-dimensional δ-phase nucleus, as a function of applied field intensity E. The dashed line shows the curve $\Delta\Phi^* = \text{const}/(E - E^*)$ with a constant factor selected by the least squares fitting.

to the a axis, where the barrier height is also reduced considerably.

Owing to long-range dipole–dipole interactions the development of the phase transformation in a single layer may depend on phase states of other layers in the same crystallite and on a volume fraction of the δ-phase in other crystallites. These effects can be analyzed in a continuum approximation by calculating internal electric fields, which are created by effective polarization charges distributed along the faces of δ-phase-containing crystallites that are perpendicular to the a axis. Our calculations have shown that the influence of electric fields induced by surrounding crystallites may be ignored in the first approximation because of the low degree of crystallinity (about 50% in PVDF[1]) and the high electric permittivity $\epsilon_A \approx 27$ of the amorphous phase.[13] In turn, the depolarization field of the crystallite itself is high only near the charged faces so that it cannot hinder the formation of the δ-phase nuclei at the most part of the area of the faces normal to the c axis remote from the charged faces. (However, this depolarization field should prevent the α–δ transformation in the vicinity of charged faces if the applied field is lower than $E = p/(\epsilon_0\epsilon_a abc) \approx 150$ MV/m. In this case residual domains of the α-phase will grow after removing the applied field so that the polarization relaxation may be observed.)

The rate of the α–δ transformation may depend on both the waiting time characterizing the formation of critical nuclei and the time during which these nuclei expand over the whole area of a single layer. The expansion of a δ-phase nucleus proceeds via the motion of a phase boundary enveloping this nucleus. Translational velocities of "one-dimensional" phase boundaries perpendicular to the crystallographic a and c axes can be evaluated on the basis of the relations derived earlier[19] for a similar process of the expansion of steps on domain walls in ferroelectric crystals. Our calculations have shown that these velocities are relatively high so that we can neglect the time during which the nucleus expands up to the layer boundary in comparison with the waiting time defined by the barrier height $\Delta\Phi^*/kT$. Therefore, we can simply assume that each nucleation event increases the volume V_δ of the δ-phase in a polymer film by an amount bL_aL_c equal to the volume of a single bilayer. It should be emphasized that the above results are a direct consequence of the fact that polymer crystallites have finite sizes not exceeding several microns.[1]

Now we can calculate the rate of the α–δ transformation in the framework of the theory of absolute reaction rates (see, for example, ref 20). We shall characterize the degree of this transformation by the dimensionless parameter $\varphi_\delta = V_\delta/V$, where V is the total volume of all crystallites in a polymer film. It should be taken into account that the number of monomolecular layers in which the δ-phase nucleation can take place decreases with increasing volume fraction φ_δ so that this number appears to be proportional to the running value $1 - \varphi_\delta(t)$ of the α-phase volume fraction in crystallites. Hence, the rate $d\varphi_\delta/dt$ of the structural transformation can be written as

$$\frac{d\varphi_\delta}{dt} = \frac{2L_a}{a}\nu e^{-\Delta\Phi^*/kT}(1 - \varphi_\delta) \tag{10}$$

where the factor $2L_a/a$ allows for the number of nucleation sites in a single monolayer and ν is the attempt frequency. From eq 10 it follows that the dependence of the δ-phase volume fraction φ_δ on time t obeys the exponential law

$$\varphi_\delta(t) = 1 - e^{-t/\tau} \tag{11}$$

Here we have introduced a characteristic time τ of the α–δ transformation being defined by the relation

$$\tau = \frac{1}{\nu}\frac{a}{2L_a}e^{\Delta\Phi^*/kT} \tag{12}$$

This characteristic time τ can be determined experimentally as the time during which the product $t\,d\varphi_\delta/dt$ reaches its maximum value in the course of the field-induced structural transformation.

In order to estimate the transition time τ theoretically we assumed that the attempt frequency ν is equal to the Debye frequency $\nu_D = 5 \times 10^{12}$ Hz, $L_a \approx 1$ μm and $\Delta\Phi^* = 42\,kT$ (see section III). With these values eq 12 gives $\tau \approx 10^2$ s in order-of-magnitude agreement with the experimental data[4] obtained under the applied field $E = 150$ mV/m at room temperature.

The theoretically-predicted field dependence of the transition time τ can be approximated by a relationship, which follows from eqs 9 and 12. It can be seen that ln τ should be inversely proportional to the difference $E - E^*$. Thus, the mechanism of the α–δ transformation involving cooperative chain rotations should manifest itself in the field dependence of the transition time having the form $\ln \tau \sim (E - E^*)^{-1}$. The measurement of such a field dependence in the course of experiments would confirm the validity of our theory.

It should be emphasized that under usual conditions of poling the kinetics of the α–δ transformation may be altered by the injection of free charges from the electrodes, which leads to a nonhomogeneous distribution of an electric field intensity across the polymer film.[21] Since in our theory this effect is ignored, the data to be compared with theoretical predictions must be taken from experiments carried out with blocking electrodes.

Finally, we note that the chain reorientations during the α–δ phase transition do not necessarily proceed via actual physical rotation of chains around their molecular axes. As shown by Lovinger,[22] the same 180° reorientation results from internal 90° rotations about every g and g' bond, which changes the conformation from $tgtg'$ to $tg'tg$. However, our general results remain equally correct for this intramolecular rotational process. The only physical parameter involved in our equations, which has different values for the above two versions of chain reorientations, is the energy γ_c. From eq 9 it follows that a version leading to a lower value of γ_c should dominate. Thus, only molecular energetic calculations can demonstrate which of the two versions—actual physical rotation or intramolecular rotational process—is realized at the α–δ transformation.

V. Conclusions

1. Owing to strong intermolecular interactions in polymer crystallites cooperative chain rotations appear to be the dominant mechanism of the field-induced α–δ-phase transition in PVDF. Only two-dimensional correlations of chain rotations should play an important role in this bulk structural transformation.

2. The volume fraction of the δ-phase in a polymer film subjected to a constant electric field is expected to increase with time according to the exponential law (11).

3. The characteristic transition time τ may be determined experimentally as the time during which the product of the transformation rate and the time reaches its maximum value. The theory predicts the field dependence of the transition time to have the form $\ln \tau \sim (E - E^*)^{-1}$.

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