Modelling of chain twist boundaries in poly(vinylidene fluoride) as a mechanism for ferroelectric polarization

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It is assumed that the process of ferroelectric polarization of the beta phase of poly(vinylidene fluoride) (PVF$_2$) in response to the action of the external electric field in direction perpendicular to the molecular axis and to the film, involves movement of the chain twist boundaries. These boundaries, at which every chain is twisted by 180 degrees, separate domains of opposite polarization. The energy barriers that are surmounted as the boundary was advanced one repeat unit were calculated and compared with the energy gained by reversing the polarization of an unfavourably oriented repeat unit in an electric field that produces polarization in PVF$_2$. It is suggested that the movement of chain twist boundaries, in contradistinction to previously postulated models in which only one chain is twisted at a time, provides a model for the poling of PVF$_2$ that is feasible energetically and kinetically. Theoretical modelling, analogous to that for Bloch wall that separates domains in magnetic materials, suggest that the process of polarization might be described either as a diffusion process or as the propagation of a soliton along the chains.

(Keywords: chain rotation; dipole reorientation; domain wall; ferroelectric polymers; polarization propagation; poling field; poling mechanism modelling; poly(vinylidene fluoride) beta phase; twist boundary)

INTRODUCTION

Two processes are involved in the creation of a macroscopically polar specimen of poly(vinyl fluoride) (PVF$_2$): mechanical extension and polarization in an externally applied electric field. Mechanical extension is employed to obtain highly aligned molecules in the all-*trans* conformation of PVF$_2$, which is commonly designated as the beta phase. An oriented film of the polar, beta phase of PVF$_2$ is shown schematically in the top part of *Figure 1*. This film has the molecules aligned but unpolarized. Evidence from X-ray diffraction indicates that it contains grains, all with the chain axes aligned parallel to the draw direction, but with the other axes randomly oriented. Some of these grains are shown in the bottom part of *Figure 1*. This Figure shows the grain boundaries and typical directions of the transverse axes. In analogy with other ferroelectric materials we suppose that each grain contains domains within which the dipoles are aligned, but in the unpolarized state the dipole moments of the different domains tend to cancel so the external moment is small. This situation is depicted in the top part of *Figure 2* which is an enlargement of the small square in *Figure 1*. In this Figure, the domains A and B are shown to be separated by a transition layer, or longitudinal wall. A polarized orientation of the dipoles is created by applying an electric field at a temperature at which the molecules can rotate by a process of the general sort described in this paper. This field is applied in the direction perpendicular to both the chain axis and the PVF$_2$ film. Usually fields in excess of 0.5 megavolt cm^{-1} are needed to create alignment of dipoles, or poling. Subsequent cooling to room temperature traps this polarization. The bottom part of

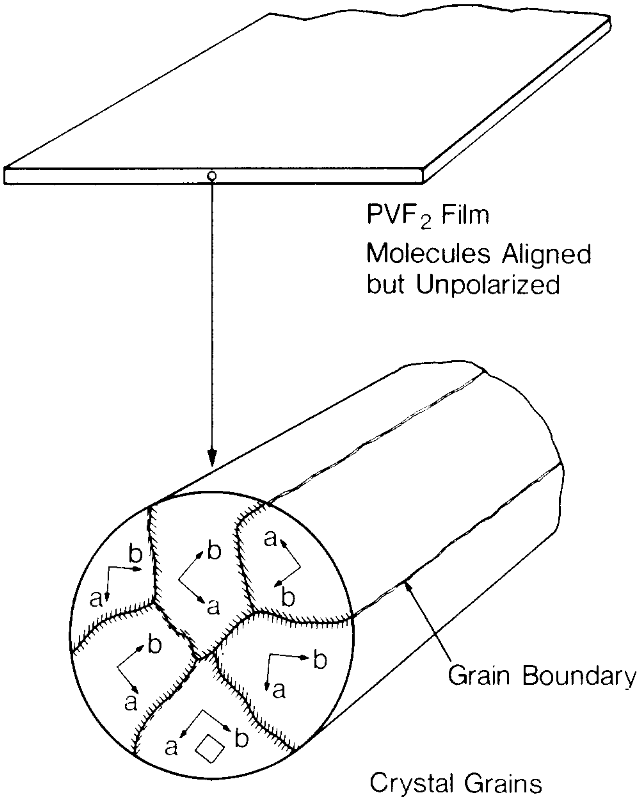

Figure 1 Top: Schematic drawing of PVF$_2$ film. Bottom: Crystal grains shown by a circled region in the top drawing, are shown in more detail. The chain axes are all parallel to the draw direction. The *a* and *b* axes transverse to the draw axis are indicated by arrows. Grain boundaries are shown by hatched lines. The small rectangle shown in the bottom of this Figure is depicted in greater detail in *Figure 2*

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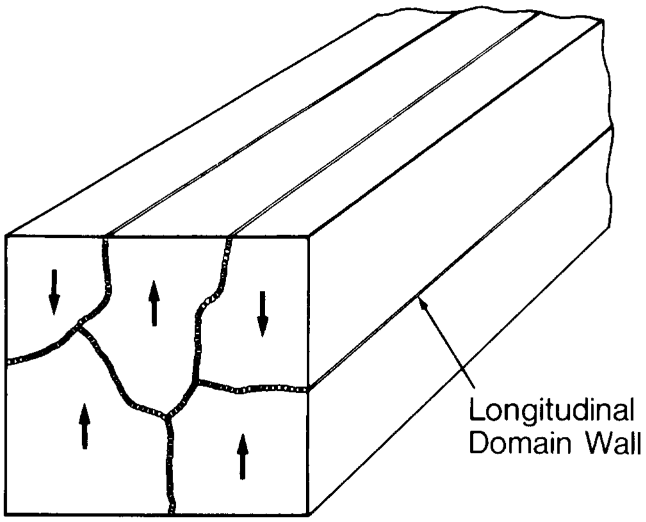
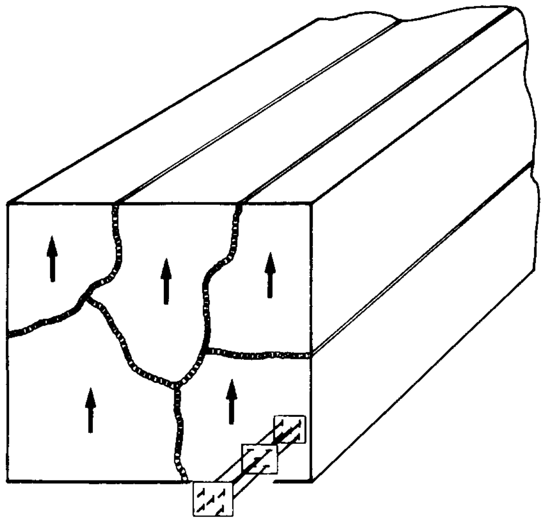


Ferroelectric Domains
Unpolarized



Ferroelectric Domains
Polarized

Figure 2 Top: Dipoles are aligned within each domain, but the random directions of polarization in adjacent domains results in no macroscopic polarization. Longitudinal domain walls are shown by irregular lines. Bottom: Same region as in top of the Figure, but in the polarized state. The drawing in the bottom right corner of this Figure shows five chains on a molecular scale. Segments of these chains containing 21 carbon atoms are detailed in *Figure 3*

Figure 2 shows schematically the ferroelectric domains in a polarized state. Measurements show that, as the polarization field cycles between positive and negative values at high temperature, the orientation of dipoles exhibits hysteresis-like behaviour. Ref. 1 summarizes the literature and provides references to the relevant experimental work. Related behaviour is observed in the dependence of the dielectric constant on the electric field. The reversal of the orientation of the dipoles in the applied field is an effect that occurs in other ferroelectric materials[2].

Different models were proposed for the polarization reversal in terms of molecular packing and structural defects. In earlier work[3,4] it was assumed that a single chain rotates 180° or by 60°. These models were investigated in more detail by Dvey–Aharon *et al.*[5]. It was suggested there that the rotation propagates as a twist wave, propagating along a single molecule near a longitudinal domain wall of the sort shown in the top part of *Figure 2* and bringing in its wake a polarization reversal. The main difficulty inherent in these models is the probable existence of a lattice misfit that increases as the twist progresses along the chain even though the part of the electrostatic energy not dependent on the external field also does not depend on the position of the twist. The extra energy arises if the rotated part of the chain does not fit into a low-energy position in the lattice. Unless there is no relative translation of the lattice on either side of the boundary (a point not examined), there will be a misfit problem for a twisted chain. Dvey-Ahron *et al.*[5] propose an alternative model in which the chain rotations proceed in 60° increments with lower barriers to rotations. This mechanism does not appear to be general since it requires a crystallographic reorientation as the domain grows and a particular orientational relationship between the domains is needed.

The model we propose here, based on the motion of chain twist boundaries which are transverse to the chain axis[6], circumvents the difficulties encountered above. Chain twist boundaries are distinct from twist boundaries associated with screw dislocation arrays in low molecular weight crystals although for brevity we frequently refer simply to 'twist boundaries' in this paper. This model is developed only for the polarization reversal in the beta phase of PVF_2. The mechanisms for poling of the alpha phase of PVF_2 are more complicated. Twist boundaries are created by processes that involve folds, chain ends, and twist-bearing crystallographic defects[6], that is, dispirations and disclinations. The creation of twist boundaries during deformation was discussed earlier[6].

In this paper it is simply assumed that, at the temperature at which poling occurs, and under the influence of the poling field, there is an appropriate supply of twist boundaries that move in a way described in this paper. Head-to-tail defects or copolymerization with poly(tetrafluoroethylene) are known to stabilize desirable crystal phases. Twist boundaries passing these configurational or chemical defects leave the same kind of desirable crystal structure behind. While such features may have a small effect on the energy of a twist boundary, it is probable that most do not seriously impede passage of the boundary.

The twist boundary which separates two domains of opposite polarization resembles a Bloch wall. A Bloch wall is a transition layer separating adjacent domains magnetized in opposite directions in ferromagnetic materials. In common with our twist boundary, the magnetic dipoles rotate in gradual increments about an axis which is perpendicular to the boundary. The energy of twist boundaries, in distinction to Bloch walls, is dominated by molecular packing considerations. Ref. 7 shows a diagram of a Bloch wall in a ferromagnet and gives a description of its behaviour.

The beta phase of PVF_2 is orthorhombic with two planar zigzag chains per unit cell. The orthorhombic cell proportions are so close to hexagonal that the structure is often referred to as pseudo-hexagonal. The pseudo-hexagonal packing differs from the true hexagonal by only 1%. Hasegawa *et al.*[8], in order to account for the observed structure factor in the X-ray diffraction pattern proposed that crystalline PVF_2 is built of chains which deviate by a small amount from a planar arrangement. The two chains in the unit cell are required to be mirror images, that is, their deviations from the perfect zigzag arrangements are of opposite sense. Since the deflection angle is small (less than 7 degrees), this arrangement could be energetically favoured over the perfect zigzag arrangement in the crystalline phase without a major effect on the energy of the twist boundary.

DESCRIPTION OF THE FORCE FIELD

The intermolecular interactions between atoms of different chains and between atoms in the same chain but separated by three or more atoms were taken from Farmer and Eby[9]. The hydrocarbon parameters in this potential function are taken from Williams (set I[10]). It should be mentioned that in the previously published work on the twist boundaries in crystalline polyethylene, similar hydrocarbon parameters based on set IV of Ref. 10 were employed. In the current calculations the data from Kobayashi, Tashiro and Tadokoro[11] were employed for the intramolecular valence force constants. These constants are for interactions for bonded atoms and for atoms bonded to a common atom. For the torsional coordinates, a slightly higher value was used, which corresponds to a torsion barrier of 10.45 kJ mol^{-1} and is the same value[6] used for polyethylene. In addition, the terminal atoms of a particular torsional coordinate are subject to non-bonded interactions (also called 1–4 interactions). These interactions are part of the intramolecular interactions between atoms separated by three or more atoms. These non-bonded intramolecular interactions are represented by the same Buckingham-type potential field used to represent intermolecular interactions. This potential results in strong repulsions between nearest F atoms on the same chain, as the F–F spacing along the chain axis (0.254 nm) is less than twice the van der Waals radius of fluorine. The extra large C–C–C and F–C–F bending constants in the valence force field used here prevents large distortions in the conformation. The dihedral angles in the planar PVF_2 were found, upon energy minimization, to deviate by less than 0.4° from the 180° values of the all-*trans* conformations. One can regard the extra energy which results from the interactions between F atoms belonging to neighbouring repeat units as an additive constant.

TWIST BOUNDARY ENERGETICS

The oligomer selected for the computations is comprised of 21 carbon atoms, with a structure $CH_3(CF_2CH_2)_9CF_2CH_3$. The chain is packed in crystallographic register with lattice constants $a = 0.858$ nm, $b = 0.491$ nm. The planar zigzag segments are packed with their dipoles pointing along the b axis. The system includes a central chain, six neighbours which comprise the inner shell and 12 more distant neighbours. In order to minimize the packing energy of the entire

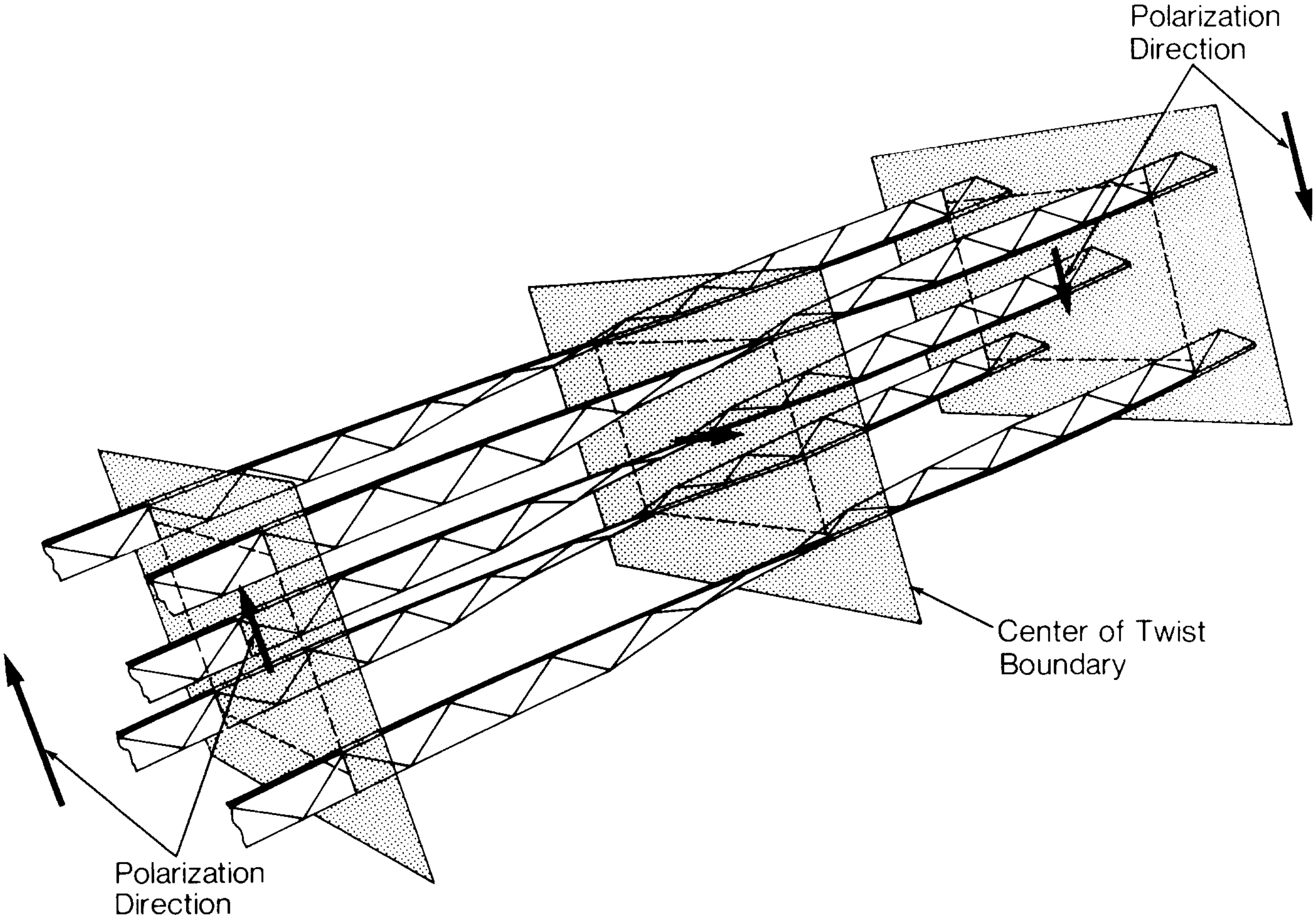


Figure 3 Twist boundaries in 5 chains are shown, with the calculated conformation. There are 21 carbon atoms between the hatched rectangles near the ends. The middle rectangle shows the location of the centre of the twist boundary. The polarization directions are shown by arrows. The direction of the dipole is reversed as the molecule passes through a twist boundary. When an external field is present, the total energy is lowered as the twist boundary moves in a direction that allows more of the dipoles attached to each molecule to align with the field

system, the Newton–Raphson algorithm for energy minimization was modified as follows: the conformation that minimized the energy of the central molecule was first determined. However, the minimization did not proceed to its completion. Instead, the adjusted conformation was placed in all the molecules and the minimization process was repeated. At the end of this process, the entire system was at its minimum packing energy, and all chains had an identical conformation. In this method the fluctuations in the atomic displacements often increase from one iteration step to another and the results can diverge. To prevent divergence, it was necessary to slow the rate of convergence by attenuating the fluctuations in the displacements.

We first calculated the total energy of the central chain in a perfect zigzag system. This energy, which includes all inter- and intramolecular interactions of the central chain was found to be $-45.31\ \text{kJ mol}^{-1}$. For the sake of comparison with existing calculations on energetics of ferroelectric polymers we recalculated this energy with exclusion of the intra F...F interactions between the nearest CF_2 groups. This energy is $-132.5\ \text{kJ mol}^{-1}$.

The twist boundary, located near the middle of the same oligomer was constructed and energy-minimized, using the numerical algorithm described above. Each chain in the system was twisted 180° in the same sense to create a twist boundary. This created a bicrystal, with the two parts of the crystal in a twin relationship and with the dipoles pointing in opposite directions on the two sides of the boundary. The twisted region was confined within a ten-bond segment, that is, it has 5 crystallographic repeat units. The twist boundary, as determined from the energy-minimization calculation, is shown in *Figure 3*. This Figure shows a central chain and 4 surrounding chains in the pseudo-hexagonal packing. Polarization directions are shown by arrows.

The total energy from all inter- and intramolecular interactions of the central twisted chain was calculated as $0.73\ \text{kJ mol}^{-1}$. The excess energy associated with the twist was therefore $46\ \text{kJ mol}^{-1}$. For comparison, the excess energy associated with the 180° twist boundary in polyethylene was found[6] to be $64.5\ \text{kJ mol}^{-1}$. The lower value here is a consequence of the force field, and also is attributed to the presence of strong intramolecular forces of repulsion between neighbouring CF_2 groups which tend to be slightly reduced by the chain twist. In the present calculations dipole–dipole electrostatic interactions are not included, since their contribution to the excess energy associated with the twist boundaries is negligible.

Table 1 Dihedral angles of moving twist boundaries at initial, intermediate and final steps

Bond #		Dihedral angles							
		Initial		End of Step 1		End of Step 2		Final	
1		180		178		179		180	
2		174		176		175		179	
3		173		176		174		178	
4		156		156		156		174	
5		158		162		159		173	
6	Twist boundary	169		175		173	Drive 6.7	158	Twist boundary
7		168		174		173		156	
8		157		157		173		169	
9		156		157		169		169	
10		169		174	Drive 10,11	152		158	
11		169		173		152		154	
12		159		175		175		169	
13		154		170		169		169	
14		176	Drive 14,15	152		153		161	
15		177		152		152		152	
16		180		178		179		174	
17		180		179		180		175	
18		180		180		180		180	

Table 1 shows the dihedral angles at each bond for the low energy conformation of the twist at the start of the drive and at the end of each of the three drive steps. Both bonds driven are changed in equal increments during each step. The final low energy conformation, similar to that at the start, is shifted by one repeat unit (2 bonds) along the chain

MOTION OF TWIST BOUNDARY

The twist boundary, as seen from *Table 1*, is built of alternating pairs of dihedral angles, one pair close to the *trans* value, the other pair closer to *gauche*. The twist region starts and terminates with a pair of dihedral angles near 155°. This remarkably ordered arrangement of the dihedral angles, which is a consequence of the particular force field for the non-bonded interactions, greatly facilitates the selection of the best stratagem to be used in order to advance the boundaries in one direction without encountering high barriers.

The technique employed in driving the twist boundary, the so-called 'bond-driving method' was described earlier[12]. The mechanism used here, which involves driving the dihedral angles at pairs of bonds in succession in the entire twist boundary differs from the mechanism of driving an isolated defect in a lattice which was used for polyethylene. The motion of the twist in PVF_2 is over relatively low energy barriers. The cooperative nature of the movements of various bonds in response to the motion of the artificially driven bond is of a much shorter range than was the case for twist bearing defects in polyethylene. A driven bond in a PVF_2 twist boundary induces a dihedral angle which is one bond removed from the driven angle to move in the opposite sense by approximately the same amount, so that the total amount of twist (180°) is preserved. Other bonds, including the one next to the driven bond, hardly change. The sequence of choosing dihedral angles to drive defines the direction in which the wall advances. The first pair of driven angles expands the thickness of the boundary. The sequence of drives shown in *Table 1* propagate the pairwise rotations through the boundary. The final step results in the rotation of the tail part of the boundary into a *trans* conformation. The boundary has now progressed by one crystal repeat unit (two bonds). One could say that this process 'works' a pair of *trans* dihedral angles from the advancing end of the boundary toward its trailing end. At the end of three cycles of this bond-driving procedure, the entire twist boundary is advanced by one repeat unit. The advanced twist has a conformation very nearly the same as its initial conformation. *Table 1* presents the dihedral angles of the system at the starting point and at the end of each one of the three driving processes. The energy of the twist boundary as a function of the driven dihedral angles is shown in *Figure 4*. This Figure shows the twist energy as a function of the dihedral angle of the driven bond for each of the three driving bond processes. As is seen in *Figure 4*, the barriers that the twist boundary must surmount do not exceed $7.5\ \text{kJ mol}^{-1}$. This estimate must be regarded as an upper bound on the barrier, for the following

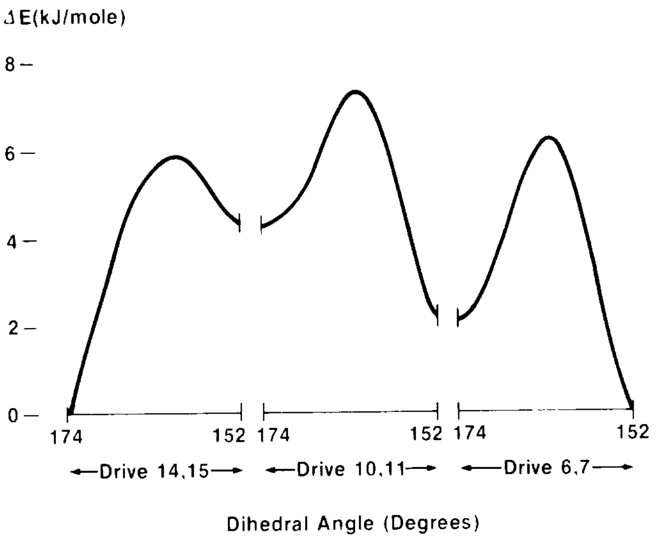


Figure 4 Twist boundary energy is plotted as a function of the dihedral angles of the driven pairs of bonds. The three stages of the driving processes are shown. They are separated by small gaps. The numbering of the driven dihedral angles is given in *Table 1*

reasons: energy minimization of an infinite system, using the method employed in this work does not guarantee that the true minimum-energy path is obtained. The algorithm used, and, in particular, the selection of the starting conformation and of the length of the iteration step, affect the minimum-energy path that the twist boundary is launched upon. Another factor that could lead to lower barriers in the true minimum-energy path is a relaxation of the lattice constants. In our computations, the lattice constants are kept fixed throughout the system. Lower barriers would be obtained if the parameters *a* and *b* in twist boundary were treated as adjustable variables during the energy minimization procedure. There are also probably mechanisms that permit the wall to advance along lines that sweep across the wall rather than as a rigid plane. Such mechanisms tend to reduce the effective barriers to wall motion.

EFFECT OF APPLIED ELECTRIC FIELD ON WALL MOTION

The literature[1] quotes the value of 7.0×10^{-30} coulomb-meter for the dipole moment per repeat unit of beta-PVF_2, in a direction normal to the chain axis. This value is strictly valid in a vacuum, or cavity. According to Frohlich[13], the continuum theory predicts that in a crystal the real moment is considerably higher. The correct moment is obtained by multiplying the vacuum moment by a factor which is equal to $(\varepsilon_\infty + 2)/3$, where ε_∞ is the dielectric constant at infinite frequency. The dipole moment per repeat unit in the uniform dielectric medium is, therefore, equal to 12.0×10^{-30} coulomb-meter. Purvis and Taylor[14] pointed out that the continuum theory is exactly valid only in uniformly polarized crystals so that it is only an approximation in beta PVF_2. The presence of domains of opposite polarization on either side of a domain wall tends to reduce this field enhancement, perhaps to zero. In an applied poling field of 2 MV cm^{-1}, the energy (dipole moment times electric field) associated with the rotation of a dipole unit is therefore within the range of 0.87 to 1.45 kJ mol^{-1}. This number is significant enough to make a large increase in the probability that the twist boundary will advance over the potential barrier (7.5 kJ mol^{-1} or less) and advance one repeat unit. If, as seems likely, nature finds a lower boundary than our somewhat arbitrary drive mechanism, the applied electric field will cause the twist boundary to advance even faster.

MODELLING OF BOUNDARY MOTION AS SOLITONS

Our calculations showed that the twist boundary moves without significantly changing its shape. Therefore, the system possesses a kind of translational invariance and can be modelled by a soliton. The single soliton corresponds to a moving wall separating two domains of opposite polarization. Hence, we model this soliton on the theory of the motion of Bloch walls in magnetic crystals. A typical Bloch wall is shown in Figure 23, Ref. 7. Ref. 15 presents a theory of Bloch walls modelled on sine-Gordon equation for solitons. The variable of this equation appropriate for PVF_2 is described in terms of Eulerian angles and it measures the amount of twist, or simply, twist[6]. The stability of the magnetic Bloch domain wall is determined from two kinds of energies: the exchange energy and the energy due to anisotropic effects[15]. In our modelling, the exchange energy is replaced by the energy associated with the interaction energy between neighbouring repeat units. The coefficient of this energy is called the elastic, or spring constant. This constant can be determined from the calculated intramolecular energy associated with each repeat unit and its dependence on the amount of twist. The anisotropy energy of the ferromagnetic domain wall is replaced by the energy that combines the energies associated with the interchain potential. The force constant associated with this potential is estimated from the excess intermolecular energy of twist boundary over that of a planar zigzag chain. It should be mentioned that the interchain energy in the twist boundary is of attraction, but the excess energy as defined here is of repulsion. The intrachain energy associated with the twist is always of repulsion.

These two energies, one associated with elastic forces, and the other with intermolecular forces balance each other leading, upon energy minimization, to the minimum energy conformation of a twist boundary.

The soliton theory of domain wall[15] allows us to compute the excess energy per unit area of the twist boundary and the width of the wall directly from the two force constants which characterize the potential energy of the boundary. The results agree well with those obtained from the twist boundary energetics, described above. Since it is of interest to model the behaviour of twist boundaries in the presence of an external electric field, external electric forces are added as external perturbations[16]*. Dissipative forces balance the driving forces which originate from the applied electric field, so that the soliton velocity approaches an asymptotic value.

The energy associated with the applied electric field in PVF_2 is much smaller than the energy associated with interchain interactions within the domain wall so it is reasonable to use the perturbation approach. In the

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* Nakajima *et al.*[17] provide numerical solutions of the soliton equation with external and dissipative forces for a large range of these parameters. Thus, a wider range of forces, where perturbation theory is not sufficiently accurate can be treated

limiting case when the energy from the polarizing field overwhelms the barrier energies, the soliton velocity reaches its maximum value.

In summary, the soliton model provides a mathematical model for various dynamic aspects of the propagating wave of electric polarization associated with a mobile twist boundary. In particular, the switching times, which are given to experimental verification[18], can be estimated as a function of the strength of the applied electric field and of the crystalline forces which affect the motion of the twist boundary. The soliton solution as outlined above leads to fast poling times and to resonance phenomena not observed. For a typical 10 nm thick lamella the poling times predicted are in nanoseconds. The observed poling times[18] are in microseconds. A plausible assumption is that the wall motion is 'impeded', 'scattered' or 'dissipated' by folds, chain ends and other structure-disrupting defects which have not yet been either modelled or experimentally measured in adequate detail. The scattering of well-defined walls thus becomes the matter of most interest for the future.

There is an alternate approach, based on the Smoluchowski diffusion equation. This was developed in Ref. 19 for the motion of a dispiration. Ref. 19 provides a general formulation for calculation of drift velocities for a defect confined between reflecting or absorbing boundaries in presence of external forces with a step function dependence on time. A similar calculation for a twist boundary would require an estimate for the mobility of the domain wall (or of the diffusion coefficient), which has to be determined independently. It can be assumed that the diffusion constant for the domain wall is higher than for the dispiration, since the twist boundary flows over lower energy barriers than point defects. The method given in Ref. 19 leads to an estimate of drift velocities as sums of velocities caused by external (electric) forces and by diffusional, or Brownian, forces. The poling times are inversely proportional to drift velocities.

Diffusion of a twist boundary also provides a useful model to describe polarization of ferroelectric polymers. The connection between the controlling microstructural features and polarization times remains to be established.

In summary, the soliton model neglects Brownian, or random, motions of the domain wall under applied forces, while the stochastic defect diffusion model overemphasizes them. Both models contain parameters not yet satisfactorily connected to microstructural features at the atomic scale.

CONCLUSIONS

The poling of the beta phase of PVF_2 was investigated in terms of the propagation of twist boundaries at which all the chains are twisted in the same sense in the pseudohexagonal lattice. The twist boundary overcomes a series of barriers to advance. The heights of the barriers were found not to exceed 7.5 $kJ\ mol^{-1}$, and are probably even lower than this. The twist boundaries advance in such a way that, after moving a distance equal to one repeat unit, the same low energy conformation recurs. Under poling conditions most commonly employed, the poling force, pE, is comparable in its magnitude to the potential barrier that the travelling twist must surmount. The results indicate that the movement of the twist boundary, in distinction to previous models which consider only one chain to twist at a time, provides a model for the poling of PVF_2 that is feasible energetically and kinetically. Additional considerations are presented which show how the dynamics of the twist boundary can be modelled by motion of a soliton or by a diffusion process.

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