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Modeling of Polymer Epitaxial Crystallization: β-Poly(vinylidene fluoride) on (111) CaF$_2$

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ABSTRACT: Molecular mechanics interaction energy calculations have been carried out in an effort to model the epitaxial behavior of the β phase of poly(vinylidene fluoride) (β-PVF$_2$) on the (111) cleavage surface of CaF$_2$. The Coulombic contribution to the total energy for this system is much higher (about 40%) than for other polymer/substrate systems that have been modeled with the same technique. The lowest energy configuration is one in which the β-PVF$_2$ chain axis is parallel to and centered over a row of fluoride ions in the substrate surface. In this energy minimum, the β-PVF$_2$ molecular dipoles are parallel to the surface. However, another low-energy configuration having the β-PVF$_2$ dipoles perpendicular to the surface exists and has an interaction free energy only 2.7% higher than the lowest energy minimum. The implications that these calculations have on the prospect of forming a piezoelectric film of β-PVF$_2$ directly via epitaxial crystallization are discussed.

Introduction

Since the first observation by Willems and Fischer,[1,2] many experimental accounts of polymer epitaxial crystallization have appeared in the literature.[3] Less numerous are theoretical or modeling studies that attempt to justify the experimentally observed polymer chain orientations and crystal structures in the epitaxial thin films. Computer modeling of the epitaxial process was first carried out by Hopfinger et al.[4-7] for polyethylene and poly(oxymethylene) on various alkali halide substrates. The molecular mechanics method was used, which involves pairwise summation of all possible polymer atom–substrate ion interactions, using molecular potential functions that represent dispersion-repulsive, Coulombic, and induced dipolar energies. The total interaction energy for a polymer segment frozen into its crystalline conformation was mapped out as a function of the orientational variables of the polymer/substrate system, and minima were located. In accord with experimental results, they found that the energetically preferred chain orientation was ⟨110⟩ on all substrates. They were also able to account for the existence of the metastable monoclinic phase in thin films (<50 Å) of polyethylene on NaCl by considering a "monolayer nucleus" consisting of seven polyethylene chain segments as the depositing species.[7] These early successes established the molecular mechanics approach as a valid predictive tool for polymer epitaxial processes. The molecular mechanics technique has been used subsequently in computer modeling studies of the epitaxial behavior of poly(sulfur nitride) on alkali halides by Mauritz et al.,[8] polyethylene on graphite by Baukema et al.,[9] poly(ethylene oxide) on nylon-6 by Hoyt et al.,[10] and poly(p-xylylene) on NaCl and KCl by Isoda[11] and to account for varying nucleation densities of poly(oxymethylene) on alkali halide substrates by Balik et al.[12]

A common characteristic of the modeling studies mentioned above is the relatively small contribution (typically less than 10%) of the Coulombic (polar) term to the total interaction energy at the global minimum for the polymer/substrate system. The dispersion-repulsive term has been found to be the major force controlling the epitaxial behavior of these systems. This is because relatively nonpolar polymers are involved, interacting with nonpolar substrates. Even the ionic alkali halides, whose (001) cleavage planes have often been used as epitaxial substrates, have an electrically neutral surface with a rapidly decaying electric field as distance from the surface increases.

In this paper we model the epitaxial behavior of a polymer/substrate system in which polar interactions play a more important role. For this purpose, the poly(vinylidene fluoride)/CaF$_2$ system has been chosen. CaF$_2$ cleaves on its (111) planes to produce a charged surface consisting entirely of F$^-$ ions, unneutralized by surface ions of opposite charge, and has not yet been considered as an epitaxial substrate for polymers. Poly(vinylidene fluoride) (PVF$_2$) is a polar polymer that has been intensively studied and characterized as a piezoelectric material. This property is dependent on the degree of molecular or dipole orientation. Epitaxial crystallization is a means for producing polymeric thin films having a high degree of chain orientation and therefore represents a potential technique for controlling and modifying the piezoelectric properties of this polymer. In order to obtain a piezoelectric film of PVF$_2$ epitaxially, the substrate must cause the C–F$_2$ dipoles to align uniformly normal to the surface. Orientation

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Table I
Potential Parameters and Contact Distances

atom pair		A_{ij}, Å^6 kcal/mol	B_{ij}, 10^{-3}Å^{12} kcal/mol	contact distance, Å
polymer	substrate			
C	Ca^{2+}	545.6	82.35	2.59
C	F^-	211.8	67.00	2.93
F	Ca^{2+}	328.0	32.94	2.42
F	F^-	127.3	28.14	2.76
H	Ca^{2+}	227.5	10.93	2.14
H	F^-	88.31	10.27	2.48

of the dipoles parallel to the surface will not result in a piezoelectric film since the net dipoles from separate crystals growing in opposite directions on the surface will cancel out. The molecular mechanics technique can distinguish between these two orientations by determining which orientation results in the lower polymer–substrate interaction energy. This work may therefore be considered as a predictive study of the epitaxial behavior of PVF_2 on CaF_2, as well as a feasibility study of the potential for producing a piezoelectric PVF_2 film epitaxially. We will restrict ourselves to consideration of the all-trans β-phase conformation of PVF_2, since this is the most polar of the five known PVF_2 polymorphs.

Methods and Theory

Molecular Energetics. Two different intermolecular potentials were considered: a Lennard-Jones 6–12 potential and a Coulombic potential, listed respectively below

$$E_{ij} = \frac{B_{ij}}{r_{ij}^{12}} - \frac{A_{ij}}{r_{ij}^{6}} \tag{1}$$

$$E_c = \frac{332.0\,(q_i q_j)}{r_{ij}} \tag{2}$$

In these equations, subscripts i and j represent polymer and substrate atoms, respectively, A_{ij} and B_{ij} are the attractive and repulsive potential constants for the ij atom pair, r_{ij} is the distance between atoms i and j, q_i and q_j their respective partial charges, and the factor 332.0 converts the units in eq 2 to kcal/mol.

The various potential constants and partial charges in eq 1 and 2 were obtained in the following manner. The attractive constants for like species, A_{ii} and A_{jj}, were obtained from the tabulated values of Hopfinger[13] for the polymer atoms and from the work of Reitz et al.[14] for the substrate ions. The A_{ij} were then determined from a geometric mean relationship

$$A_{ij} = (A_{ii}A_{jj})^{1/2} \tag{3}$$

The B_{ij} are found from eq 1 and the A_{ij} by constraining E_{ij} to be a minimum at the contact distance between each atom–atom pair. The contact distance is defined here as the sum of the contact radius of the polymer atom (from ref 13) and the ionic radius of the substrate ion. Contact distances and potential constants for each atom–atom pair are listed in Table I.

The substrate ions have been treated as point charges, having valences −1 and +2 for F and Ca, respectively. The partial charges q_i for the polymer atoms were taken from ref 15 for the all-trans (β-phase) conformation of PVF_2 and were computed with the CNDO/2 closed-shell molecular orbital scheme.[16] The partial charges used here are: $q(\mathrm{H}) = +0.045$, $q(\mathrm{F}) = -0.215$, $q(\mathrm{C\ bonded\ to\ H_2}) = -0.021$, and $q(\mathrm{C\ bonded\ to\ F_2}) = +0.361$ eu.

Induced dipolar energies for polymer/alkali halide substrate systems have been repeatedly found to be more or less independent of polymer orientation.[4,5] This is especially true for polymers containing atoms with low polarizabilities, as is the case for PVF_2. Induced dipolar energies have therefore not been included in these calculations.

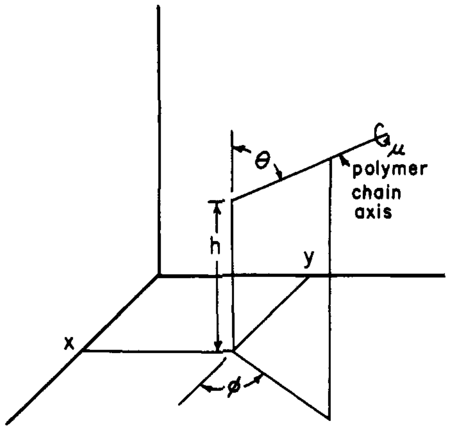

Figure 1. Spatial parameters used to describe polymer/substrate geometry. The CaF_2 (111) surface plane is xy, the origin of the coordinate system is at a fluoride ion, and the x axis is oriented along a row of fluoride ions. Height (h) above the surface is measured from the polymer atoms that are closest to the surface.

Molecular Geometry. A PVF_2 segment consisting of 10 repeat units (60 atoms) frozen into the all-trans β-phase conformation was taken as the depositing species. Bond lengths and angles were taken from ref 15.

The (111) cleavage plane of CaF_2, consisting of fluoride ions packed hexagonally, was taken as the substrate surface plane. The stacking sequence for CaF_2, in the [111]direction, consists of alternating hexagonally packed planes of fluoride and calcium ions, grouped in electrically neutral layers of three planes (F–Ca–F), with an interplanar spacing of 0.787 Å. These layers are separated by a gap equal to twice the interplanar spacing. There are three such three-plane layers in the CaF_2 unit cell along the [111]direction.

In general, six positional and orientational parameters are required to completely define the spatial relationship between polymer and substrate (see Figure 1). These include translation of a point on the end of the polymer chain axis along each of the three Cartesian axes in the substrate reference frame (x, y, h, h is the height above the surface), rotation of the polymer about its own chain axis (μ), rotation of the polymer chain axis about the normal to the substrate surface (ϕ), and the angle that the polymer chain axis makes with a normal to the substrate surface (θ). Nonparallel alignment of the polymer chain axis with the substrate surface results in much higher interaction energy states than does parallel alignment, therefore θ has been held constant at 90°. It has also been found experimentally that the polymer chains are oriented parallel to the substrate in most epitaxial thin films. This study has therefore been limited to studying the interaction energy hypersurface as a function of the remaining five variables.

Three different rotational positions about the polymer chain axis have been considered and are illustrated in Figure 2. $\mu = 0°$ corresponds to having the fluorine atoms of the polymer next to the substrate (orientation 1, CF_2 dipoles are normal to the surface), $\mu = 90°$ corresponds to having the plane of the planar zigzag carbon chain parallel to the substrate (orientation 2, CF_2 dipoles are parallel to the surface), and $\mu = 180°$ corresponds to having the hydrogen atoms next to the substrate (orientation 3, CF_2 dipoles are normal to the surface). From the standpoint of forming a piezoelectric film, either orientation 1 or 3

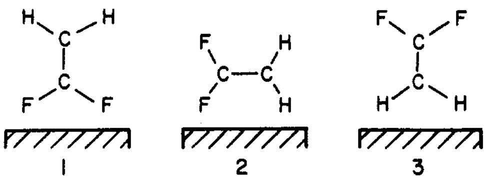

Figure 2. Three chain axis orientations considered in this work. Orientations 1, 2, and 3 correspond respectively to $\mu = 0°, 90°$, and 180°. The β-PVF$_2$ dipole moment is normal to the surface in orientations 1 and 3 and parallel to the surface in orientation 2.

would produce the required normal orientation of the CF$_2$ dipoles.

Summation Technique. The total polymer–substrate interaction energy is determined by summing eq 1 and 2 over all possible polymer atom–substrate ion pairs, for each position and orientation of the polymer segment with respect to the substrate. This problem essentially reduces to evaluation of sums of the type $\sum 1/r^n$, where $n = 1$, 6, or 12, and rapidly convergent expressions for determination of these sums are desirable. The Ewald sum technique is particularly useful for this purpose.[17] For a single polymer atom interacting with a single plane of substrate ions, the relevant expressions are

$$\sum 1/r = \frac{1}{A}\sum|\mathbf{k}_h| \exp(2\pi h|\mathbf{k}_h| + 2\pi i\mathbf{k}_h\cdot\mathbf{r}) \qquad (4)$$

$$\sum 1/r^6 = \frac{\pi}{2Ah^4} + \frac{\pi^3}{Ah^2}\sum|\mathbf{k}_h|^2 K_2(2\pi h|\mathbf{k}_h|) \exp(2\pi i\mathbf{k}_h\cdot\mathbf{r}) \qquad (5)$$

$$\sum 1/r^{12} = \frac{\pi}{5Ah^{10}} + \frac{\pi^6}{60Ah^5}\sum|\mathbf{k}_h|^5 K_5(2\pi h|\mathbf{k}_h|) \exp(2\pi i\mathbf{k}_h\cdot\mathbf{r}) \qquad (6)$$

In these expressions A is the area of the substrate unit cell, h is the height of the polymer atom above the substrate surface, $\mathbf{k}_h$ is an arbitrary vector in the reciprocal lattice of the substrate, $\mathbf{r}$ is the component of the position vector of the polymer atom in the space of the substrate lattice, and K_2 and K_5 represent second- and fifth-order modified Bessel functions of the second kind, respectively. The sums are taken over all values of $\mathbf{k}_h$ and are truncated when the relative contribution of the last term to the sum is negligible. In practice, the rapid decay of the Bessel functions causes this to occur after only a few terms. The rest of the substrate is accounted for by incrementing h for the next plane of substrate atoms and repeating the calculation. Substrate planes are always added on in groups of three (F–Ca–F) to maintain electrical neutrality for the entire substrate and to ensure convergence of the Coulombic term. This is continued until the relative contribution of the last group of three planes to the total sum is negligible. In practice, the series was truncated when the last F–Ca–F layer accounted for less than 0.01% of the total interaction energy. With this scheme, computation of the total interaction energy for a single atom interacting with an infinite 3-dimensional CaF$_2$ substrate bounded by a (111) surface plane takes approximately 250 ms on a VAX 11/750.

Contour Plots. Following Mauritz,[4,5] results have been plotted as isoenergy contour maps with h and ϕ as independent variables, at fixed values of x, y, an μ. The origin of the coordinate system is taken at a fluoride ion in the surface, and $\phi = 0$ corresponds to having the β-PVF$_2$ chain axis centered over and parallel to a row of fluoride ions, i.e., along the substrate $\langle\bar{1}10\rangle$ directions. The contour plots were obtaned by computing the interaction energy at heights ranging from 1 to 4 Å, in 0.1-Å steps, and at rotation angles (ϕ) ranging from 0 to 120°, in 10-deg steps. Height above the substrate is measured from the polymer atoms that are closet to the surface. Isoenergy contour lines are scaled in (kcal/mol)/10 PVF$_2$ repeat units above the minimum energy for each contour plot.

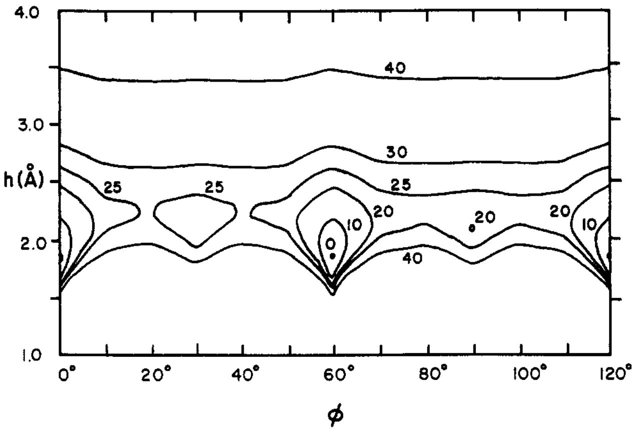

Figure 3. Energy contours in (kcal/mol/10 PVF$_2$ repeat units above the absolute minimum for orientation 1 with $(x, y, \mu, \theta) = (0, 0, 0°, 90°)$.

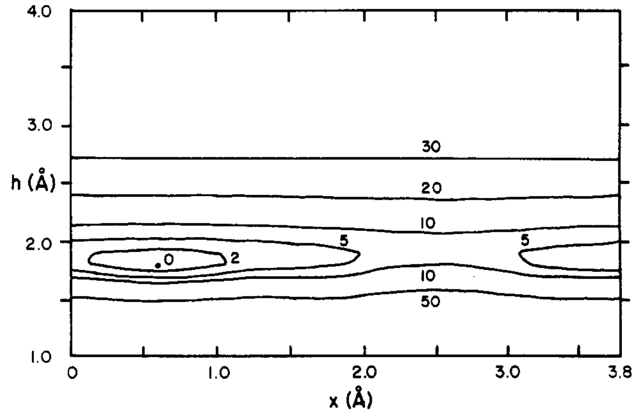

Figure 4. Energy contours in (kcal/mol)/10 PVF$_2$ repeat units above the absolute minimum for translation along a row of fluoride ions (x) with $(y, \phi, \mu, \theta) = (0, 0°, 0°, 90°)$. The distance between adjacent fluoride ions on the substrate surface is about 3.8 Å.

Results

A typical plot is displayed in Figure 3, which represents the case $(x, y, \mu, \theta) = (0, 0, 0°, 90°)$ and corresponds to orientation 1 with the first carbon atom in the β-PVF$_2$ chain centered over a fluoride ion in the substrate. Steep potential energy wells are located at 60° multiples of ϕ. The positions of these minima did not change when several other values of x and y were tried, although the magnitude of the minimum energy changed. The absolute (global) minimum energy for this orientation was determined by holding ϕ constant at one of its minimum energy values (e.g., 0°) and translating the β-PVF$_2$ chain in 0.1-Å increments along this direction, parallel to and centered over a row of fluoride ions in the substrate. The resulting h vs. x contour plot is shown in Figure 4. This energy surface is relatively smooth, with a shallow minimum located at 0.6 Å from a fluoride ion. Similarly smooth contour plots were obtained when this procedure was applied to orientations 2 and 3; the same h–ϕ and h–x minima were found for orientation 2 as were found for orientation 1. The h–ϕ energy minima for orientation 3 occurred at $\phi = 30°$ and 90°, and the h–x minimum occurred at $x = 1.0$ Å.

The final h vs. ϕ contour plots chosen for discussion are those obtained by setting x and y equal to the values found

Table II

Absolute Minimum Energies, Minimum Energy Heights, and Thermodynamic Parameters from Contour Plots

figure	total energy[a]		dis-rep energy[a]		% Coulombic energy at min	entropy[b]	free energy[c]
	E_{min}	h_{min}, Å	E_{min}	h_{min}, Å			
5	-53.4	1.8	-34.0	2.0	42	2.76	-54.6
6	-55.4	1.6	-36.8	1.8	41	1.56	-56.1
7	-35.2	1.9	-35.5	1.9	0.8	4.97	-37.4

[a] Units are (kcal/mol)/10 PVF_2 repeat units. [b] Units are (cal/mol·°K)/10 PVF_2 repeat units; see text for explanation. [c] Units are (kcal/mol)/10 PVF_2 repeat units; see text for explanation.

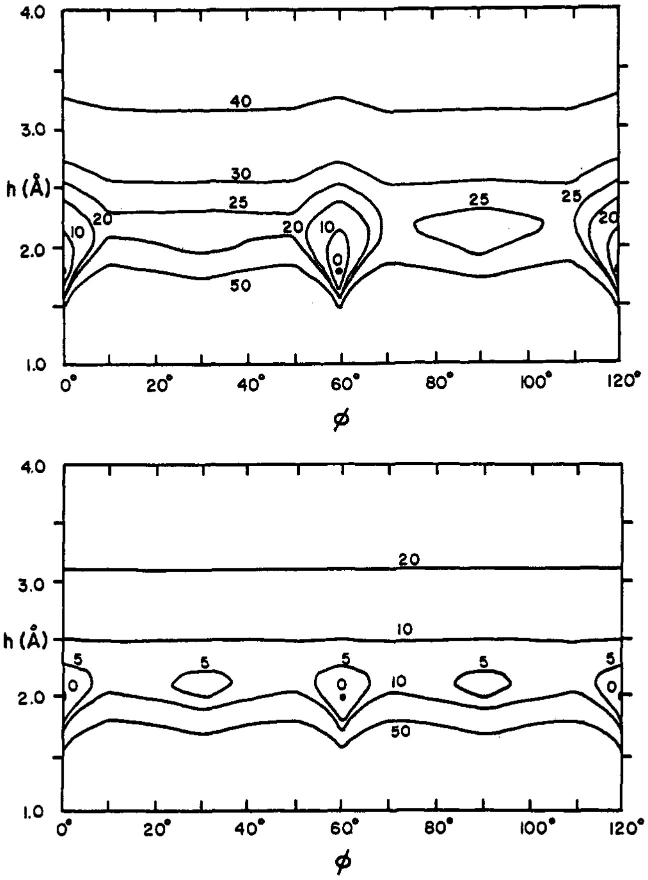

Figure 5. Energy contours in (kcal/mol)/10 PVF_2 repeat units above the absolute minimum for orientation 1 with $(x, y, \mu, \theta) = (0.6, 0, 0°, 90°)$. Upper plot, total interaction energy; lower plot, dispersion-repulsive energy only.

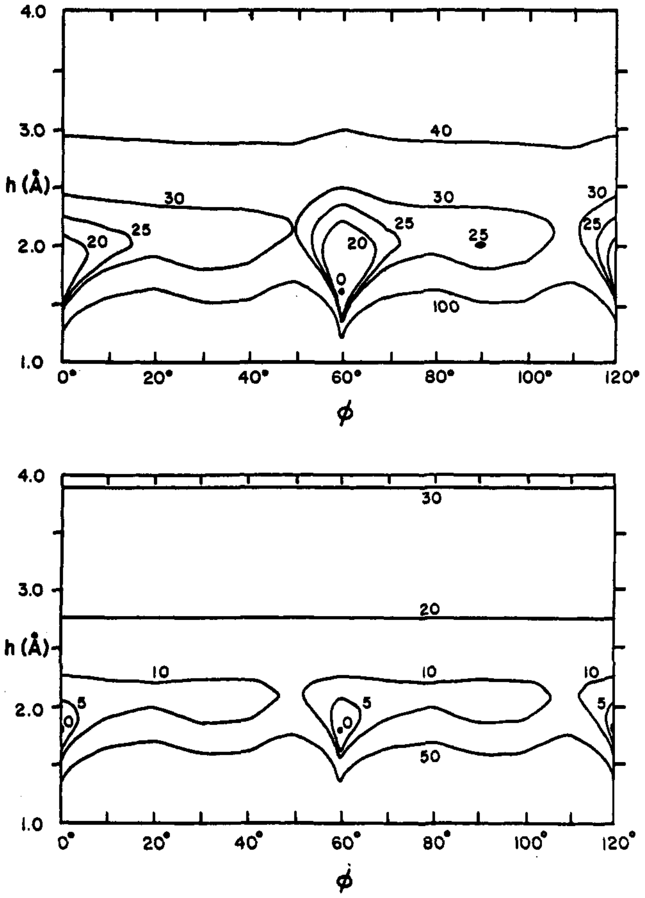

Figure 6. Energy contours in (kcal/mol)/10 PVF_2 repeat units above the absolute minimum for orientation 2 with $(x, y, \mu, \theta) = (0.6, 0, 90°, 90°)$. Upper plot, total interaction energy; lower plot, dispersion-repulsive energy only.

for the translational minimum, as illustrated in Figure 4, for each orientation. The resulting contour plots therefore represent that $h\phi$ plane that contains the global energy minimum for each particular β-PVF_2 chain orientation. These results are displayed in Figures 5–7. The upper plot in each figure represents the total interaction energy, whereas the lower plot is the dispersion-repulsive energy only, and a comparison of the two illustrates the effect of the Coulombic term on the energy surface. Global energy minima and other data corresponding to the energy contour plots have been listed in Table II. Schematic illustrations of a three-repeat-unit segment of β-PVF_2 in its minimum energy position for each orientation are shown in Figures 8–10.

Comparison of the data in Table II and Figures 5–7 shows that orientations 1 and 2 are strongly preferred energetically over orientation 3 by nearly 20 (kcal/mol)/10 repeat units. The h–ϕ energy surfaces for orientations 1 and 2 contain deep potential energy troughs at multiples of 60°, corresponding to $\langle\bar{1}10\rangle$ chain orientation. The global energy minimum values for these two orientations are very similar, although the value for orientation 2 is slightly lower by 2.0 (kcal/mol)/10 repeat units. The total interaction energy minimum is periodic every 60° for orientation 1, whereas the corresponding minimum for orientation 2 is periodic every 120°. (The local minimum at $\phi = 0°$ and 120° in Figure 6 is 10 (kcal/mol)/10 repeat units higher than the global minimum at $\phi = 60°$.) This is purely an effect of the Coulombic term, since the dispersion-repulsive contour plots for both orientations contain minima that are periodic every 60°.

The physical reason for this result can be seen in Figures 8 and 9. For orientation 1 (Figure 8), the same polymer atom/substrate ion contacts are made at $\phi = 0°$ or 60°, due to the mirror plane of symmetry for the polymer segment that contains the chain axis and is normal to the surface. Thus, the same interaction energy is obtained in both positions. This symmetry element is absent in orientation 2, and the primary effect of this is felt in the Coulombic term. At $\phi = 0°$ in Figure 9, the flourine atoms of the polymer are aligned parallel to a row of fluoride ions located 1.57 Å below the surface. The hydrogen atoms of the polymer are similarly aligned parallel to a row of calcium ions located 0.78 Å below the surface. These are unfavorable Coulombic interactions, since both involve

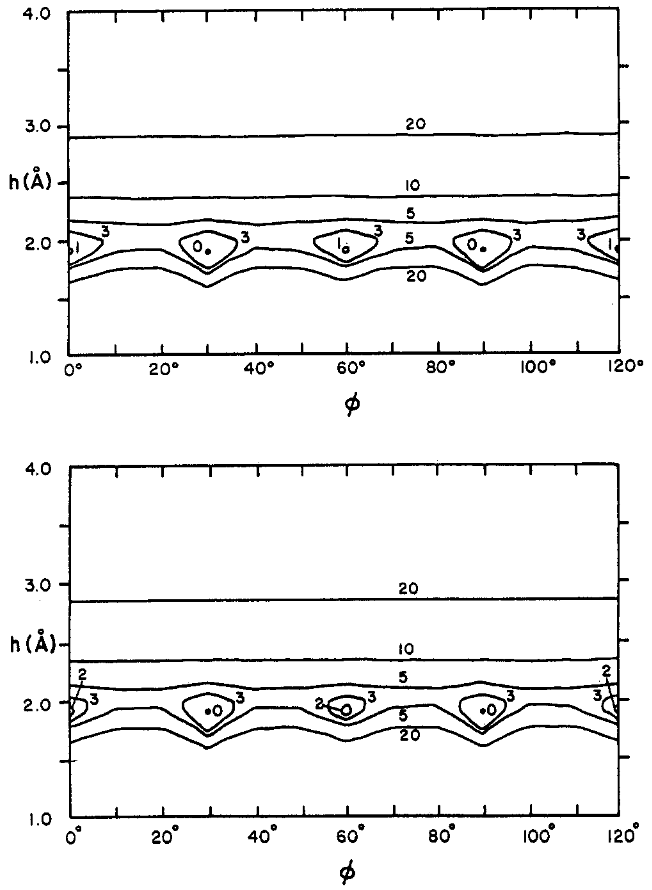

Figure 7. Energy contours in (kcal/mol)/10 PVF_2 repeat units above the absolute minimum for orientation 3 with $(x, y, \mu, \theta) = (1.0, 0, 180°, 90°)$. Upper plot, total interaction energy; lower plot, dispersion-repulsive energy only.

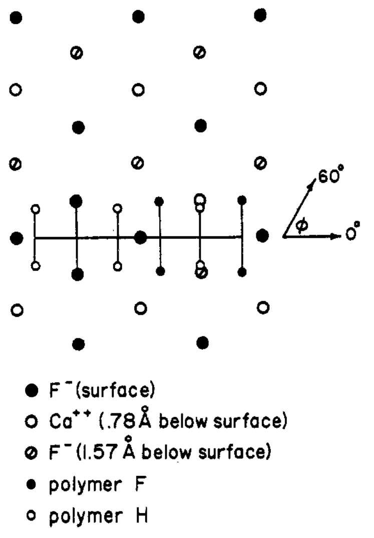

Figure 8. Schematic illustration of a three-repeat-unit segment of β-PVF_2 in the absolute minimum energy position over the (111) CaF_2 surface for orientation 1. Atom diameters are not drawn to scale.

pairs of like charges. However, rotation of the polymer segment by 60° reverses the contacts made by the flourine and hydrogen atoms of the polymer with the substrate ions, so that pairs of unlike charges are aligned parallel. This results in a very favorable Coulombic interaction. The dispersion-repulsive energies for $\phi = 0°$ and 60° are the same (refer to Figure 5) since the differences in the two positions involve subsurface atoms that are too far from the polymer segment to make a major contribution to the (short-range) dispersion-repulsive term.

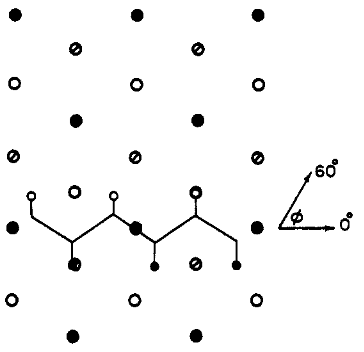

Figure 9. Schematic illustration of a three-repeat-unit segment of β-PVF_2 in the absolute minimum energy position over the (111) CaF_2 surface for orientation 2. Atom diameters are not drawn to scale. See Figure 8 for legend.

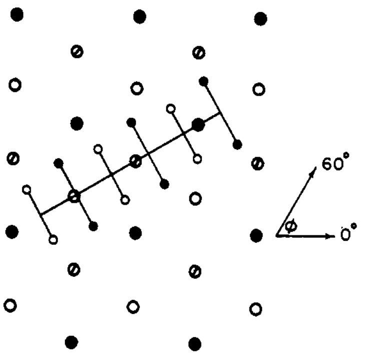

Figure 10. Schemic illustration of a three-repeat-unit segment of β-PVF_2 in the absolute minimum energy position over the (111) CaF_2 surface for orientation 3. Atom diameters are not drawn to scale. See Figure 8 for legend.

The h–ϕ energy surface for orientation 3 in Figure 7 is relatively smooth, with shallow minima located at $\phi = 30°$ and 90°, corresponding to $\langle 1\bar{2}1 \rangle$ chain alignment. Local minima, only 1 (kcal/mol)/10 repeat units higher in energy, are also present at $\phi = 0$, 60, and 120°. Very little difference is seen between the dispersion-repulsive and total interaction energy contour plots for this orientation, illustrating the almost negligible contribution of Coulombic interactions when the hydrogen atoms of the polymer are placed next to the surface. The polymer/substrate geometries corresponding to the $\phi = 0°$ and $\phi = 30°$ minima for orientation 3 can be compared with Figures 8 and 10, respectively. The reason for the close similarity in the interaction energies for these two positions is not apparent in Figures 8 and 10. Generally it may be said that the dominance of the dispersion-repulsive energy and the relatively small contribution to this energy made by hydrogen/substrate ion pair interactions (e.g., compare the A_{ij} constants in Table I) are contributing factors.

The first four columns of Table II list the minimum energies and heights at which the minima occur for both the total interaction energy plots and the dispersion-repulsive plots. The height at which the minimum occurs in the total energy is 0.2 Å lower than the height for the minimum in the dispersion-repulsive energy, for orientations 1 and 2, a reflection of strong Coulombic interactions that tend to pull the polymer closer to the surface. This Coulombic attraction is apparently strong enough to overcome steric repulsive forces arising from electron cloud overlap between polymer and substrate atoms, since the minimum energy height of the polymer above the surface for all three orientations is less than the minimum contact distance listed in Table I.

The Coulombic contribution to the total interaction energy at the minimum is over 40% for both orientations

1 and 2, a much larger contribution than has been reported for other polymers whose epitaxial behavior has been modeled with this approach. This is clearly due to the polar nature of β-PVF$_2$ and the proximity of the carbon and fluorine atoms to the surface in orientations 1 and 2. The Coulombic term is much less significant for orientation 3, in which the hydrogen atoms, containing a partial charge almost an order of magnitude lower than the carbon and fluorine atoms, are next to the surface. In this case, the minima in both the total and dispersion-repulsive plots occur at the same height, and the Coulombic contribution, although negligible, is slightly repulsive.

Discussion

The results of these calculations predict that epitaxial films of β-PVF$_2$ on CaF$_2$ should consist of polymer molecules whose chain axes are oriented in the three $\langle\bar{1}10\rangle$ directions on the CaF$_2$ (111) surface. If the long axis of the epitaxial crystallites is perpendicular to the chain axis direction, as is usually the case, the crystallites should be oriented in three equivalent directions on the surface, separated by 120°. Furthermore, either orientation 1 or orientation 2 should be obtained, with orientation 2 having a slight energetic preference. However, the most stable orientation for the system is not strictly determined through minimization of the internal energy, as has been done here, but rather through minimization of the free energy, which includes entropy effects. The entropy is related to the probability that the polymer will encounter a potential energy minimum. This factor obviously favors orientation 1 over orientation 2, since the absolute energy minima in Figure 5 occur twice as frequently as those in Figure 6. The entropy contribution can be quantitatively determined by considering the set of interaction energies for a given h–ϕ contour plot to be the available set of energy states for that orientation, and applying the formalism of statistical mechanics. The h–ϕ set of interaction energies from each contour plot is comprised of a relatively coarse grid of 372 points. However, use of a finer grid of 1860 points, generated by decreasing the ϕ increment from 10° to 2°, resulted in a difference of less than 0.02% in the computed entropy. The smaller set of interaction energies is therefore considered to be statistically representative for the purpose of computing the entropy. It should be noted that the thermodynamic quantities obtained this way cannot be considered to be accurate in an absolute sense but can be used to make relative comparisons between the various orientations of the polymer/substrate system.

The probability, P_i, of obtaining energy state E_i in the canonical ensemble, is given by the Boltzmann expression

$$P_i = \frac{e^{-E_i/RT}}{\sum_i e^{-E_i/RT}} \tag{7}$$

where T is the absolute temperature, R is the gas constant, and the sum is taken over all states. The entropy follows as

$$S = -R\sum_i P_i \ln P_i \tag{8}$$

The Helmholtz free energy, F, can then be obtained from $F = E - TS$, where E is the minimum internal energy for each orientation, as listed in Table II. The results of these calculations are displayed in the last two columns of Table II. A temperature of 170 °C was chosen for these calculations, which is close to the melting point of β-PVF$_2$, and would be typical for a melt epitaxial crystallization experiment.

As expected, the entropy contribution for orientation 1 is larger than that for orientation 2 by a factor close to 2. This results in a free energy difference between these two orientations of 1.5 (kcal/mol)/10 repeat units, with orientation 2 still being favored. This is somewhat less than the difference in the respective minimum internal energies, which amounts to 2.0 (kcal/mol)/10 repeat units. Orientation 3 has the highest entropy, because there are a large number of states with energies close to the minimum, as seen in Figure 7. However, the entropy effect is still too small to substantially change the energetic preference of this orientation relative to the other two.

Although not illustrated here, an h–μ contour plot has been constructed with $(x, y, \phi, \theta) = (0.6, 0, 0°, 90°)$ to determine the magnitude of the energy barriers for transforming between orientations 1, 2, and 3 via rotation about the chain axis. An energy barrier in excess of 30 (kcal/mol)/10 repeat units exists between orientations 1 and 2, whereas the barrier between orientations 3 and 2 is about 10 (kcal/mol)/10 repeat units. The difference in barrier heights is a result of the inherent higher energy of orientation 3 relative to the other two. At temperatures sufficiently below the melting point, it is therefore unlikely that the polymer could readjust from a higher energy local minimum (i.e., orientation 1 or 3) to the global minimum (orientation 2) through rotation about the chain axis, while maintaining ϕ constant at some multiple of 60°, since the energy barriers involved are prohibitively high.

From the standpoint of forming a piezoelectric film of β-PVF$_2$ on CaF$_2$ epitaxially, the energetic preference is toward parallel orientation of the β-PVF$_2$ dipoles with the surface (orientation 2). An epitaxial film of β-PVF$_2$ in this orientation would have a net zero dipole moment, since the individual moments from crystallites oriented in the three equivalent directions on the surface would cancel. Orientations 1 or 3, which would result in uniform dipole alignment, *independent* of crystallite orientation on the substrate, are most desirable for formation of a piezoelectric film. The large energetic preference of orientation 1 over orientation 3 makes it highly improbable for a β-PVF$_2$ chain segment to deposit in orientation 3. This is essential to formation of a piezoelectric film, since a statistical (50:50) mixture of these two orientations in the film would again result in a zero net dipole moment. A crude estimate of the distribution of polymer chain segments among the remaining two orientational states can be obtained, assuming again that Boltzmann statistics apply. The ensemble is restricted to those interaction energies corresponding to $\phi = 60°$ for orientations 1 and 2 since this will include the minimum energies for each orientation, and these will be the major contributors to the Boltzmann average. A more realistic estimate of this distribution would include in the ensemble interaction energy states generated by allowing each of the six spatial parameters to vary in small increments about the global minimum for each orientation. These more extensive calculations have not been performed, but should not change the general conclusion to be drawn here. Within the above assumptions, the number of fraction n_i of chain segments in orientation i is given by

$$n_i = \frac{g_i \sum_j \exp(-E_{ij}/RT)}{\sum_{ij} \exp(-E_{ij}/RT)} \tag{9}$$

where E_{ij} represents the jth interaction energy from orientation i, and g_i is a degeneracy factor that represents the fact that energy minima occur twice as often in h–ϕ space for orientation 1. At $T = 170$ °C, $n_1 = 0.14$ and $n_2 = 0.86$.

These calculations therefore suggest that a significant portion (roughly 14%) of the epitaxial β-PVF_2 film will be spontaneously piezoelectric, as dipoles from those segments in orientation 2 will tend to cancel, whereas those in orientation 1 will add. Other substrates having the CaF_2 structure, such as SrF_2 and BaF_2, may exhibit a different energetic preference for these two orientations. Consideration of other substrates will be the subject of a future publication.

There are, of course, other factors that could affect the dipole orientation in the epitaxial film beyond the simple, single-chain interaction energy calculations presented here. It has been assumed that the PVF_2 chain is frozen in the all-trans conformation. The interaction energies of the other two known chain conformations should be obtained and compared with the all-trans conformation, to determine whether the all-trans conformation is energetically preferred. The relatively large contribution of the Coulombic energy for the PVF_2/CaF_2 system would seem to favor the all-trans conformation over the others, since it has the largest net molecular dipole moment. The effect of neighboring chains on the dipole orientation of any single chain might also be important, due to strong polymer–polymer interactions. These effects can be taken into account by computing the interaction energy of a depositing "nucleus" of several PVF_2 chain segments, including pairwise interactions between the polymer atoms, as well as between polymer and substrate atoms. These and other related investigations are currently in progress.

Conclusions

Single-chain interaction energy calculations have been carried out for PVF_2 frozen into the all-trans conformation and a CaF_2 substrate bounded by a (111) plane. Polar (Coulombic) effects represent a larger fraction (over 40%) of the total interaction energy for this system than for the other polymer/substrate systems whose epitaxial behavior has been modeled. Comparison of total interaction energy surfaces with those generated from dispersion-repulsive potentials only shows that the Coulombic term sharpens the potential energy wells considerably. These calculations predict that epitaxial films of β-PVF_2 on (111) CaF_2 should consist of crystallites oriented in three directions on the surface spaced 120° apart, the polymer chains within the crystallites having their chain axes parallel to the $\langle \bar{1}10 \rangle$ substrate directions and centered over a row of fluoride ions. Such films should consist of a mixture of chains having parallel and perpendiculr dipole orientations with respect to the surface, the relative amounts of each being roughly determined by their respective minimum interaction energies. The interaction free energy of the parallel orientation is lower by 2.7%, suggesting that the majority of the β-PVF_2 chain segments should exist in the parallel orientation. Molecular dipoles from chain segments in this orientation will cancel, due to the equal probability of polymer chain alignment in each of the $\langle \bar{1}10 \rangle$ substrate directions. Dipole moments from regions of perpendicular dipole orientation will add since this dipolar arrangement is independent of chain axis orientation parallel to the substrate, suggesting that some spontaneous piezoelectric activity should be observed for epitaxial films of β-PVF_2 on CaF_2.

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Registry No. CaF_2, 7789-75-5; PVF_2, 24937-79-9.

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