First-Principles Study of the $\alpha$–$\beta$ Phase Transition of Ferroelectric Poly(vinylidene difluoride): Observation of Multiple Transition Pathways

Won June Kim,† Myung Hoon Han,† Young-Han Shin,‡ Hyungjun Kim,§ and Eok Kyun Lee*†

†Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
‡Department of Physics and Chemistry and ESHRC, University of Ulsan, Ulsan 680-749, Korea
§Graduate School of EEWS, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea

ABSTRACT: Transition routes from the $\alpha$ (nonpolar) phase to the $\beta$ (polar) phase of poly(vinylidene difluoride) (PVDF) are investigated by first-principles simulation methods. Among various possible routes, including complex torsional and rotational motions, we propose two prototypical transition routes and identify important intermediate structures along each transition pathway using the generalized solid-state nudged elastic band (G-SSNEB) method. The effect of the external electric field and mechanical drawing on the transition behavior is investigated by estimating electric enthalpy and stress tensors. Finite-temperature $ab$ initio molecular dynamics (AIMD) simulations and stress tensor analysis reveal the possibility of enhancement of the crystallinity under hydrodynamic compression.

INTRODUCTION

Polyvinylidene difluoride (PVDF) is the first organic material that has ferro-, piezo-, and pyroelectric properties. Because it is lead-free and flexible, it has been applied in sensors and actuators as thin film structures. The most widely used composition of PVDF is its copolymer with 20–50 mol % of trifluoroethylene (TrFE) because of its low ferroelectric Curie temperature of 340–420 K (below the melting point of the copolymer) and better piezoelectric responses compared with pure PVDF. Recent studies on PVDF and its copolymers have focused on the kinetics of fast ferroelectric switching, nonlinear dielectric response, applications for ultracapacitors, and for the building blocks in multiferroic composite materials.

PVDF has five crystalline phases according to their different intrachain conformations and chain stacking modes, which are denoted as $\alpha$ ($\text{II}_{\text{auw}}$ $\text{II}_{\text{ad}}$), $\beta$ ($\text{I}_p$), $\gamma$ ($\text{III}_{\text{pur}}$ $\text{III}_{\text{psd}}$), $\delta$ ($\text{II}_{\text{pur}}$ $\text{II}_{\text{psd}}$), and $\epsilon$ ($\text{II}_{\text{auw}}$ $\text{III}_{\text{au}}$). The I, II, and III in parentheses specify all-trans, trans–gauche–trans–gauche’ (tgg′), and trans–trans–trans–trans–trans–gauche’ (tttgg′) intrachain conformations, respectively. Subscripts in these notations describe the stacking mode of PVDF chains, where “u” and “p” represent antiparallel (nonpolar) and parallel (polar) orientations of the dipole moments between neighboring chains, and “a” and “d” represent up–up and up–down orientations along the chain direction between neighboring chains. According to these notations, the $\alpha$ and $\epsilon$ phases are nonpolar phases, and the $\beta$, $\gamma$, and $\delta$ phases are polar phases. Among the polar phases, the $\beta$ phase has the largest polarization due to its all-trans conformation. However, the nonpolar $\alpha$ phase is experimentally an in-preparation phase, and mechanical drawing or an external field is required to transform the $\alpha$ phase into the $\beta$ phase.

Many experimental studies have focused on the behavior and efficient conditions for $\alpha$–$\beta$ phase transition and on the role of the mechanical drawing and electric poling processes. The analysis of the contents of the $\beta$ phase and crystallinity has revealed that, although conformational transformation of the gauche into the trans can be done almost completely without difficulty, the $\beta$ phase still has low crystallinity. Most theoretical studies, using force field (FF) methods and density-functional theory (DFT), have focused on the analysis of the phase stability and ferro- or piezoelectric properties. Current interest has been focused on understanding the dynamics associated with $\alpha$–$\beta$ phase transition, which requires careful investigation of complicated torsional and rotational motions along the $\alpha$–$\beta$ transition route.

Because macroscopic polarization is mainly governed by the crystallinity of the $\beta$ phase, understanding the effect of the external conditions on the $\alpha$–$\beta$ transition is an important issue in manufacturing high-quality ferroelectric PVDF. In the present study, we focused on the identification of possible transition pathways connecting the $\alpha$ phase with the $\beta$ phase (the minimum energy paths (MEPs)) in bulk PVDF by using the generalized solid-state nudged elastic band (G-SSNEB) method. Energy profiles of the intermediate structures along the transition routes were obtained from the G-SSNEB calculations. The role of mechanical stretching as well as that of external electric fields were studied by estimating stress tensors and modification of the energy profile along each route, respectively. Finally, we used finite-temperature $ab$ initio

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molecular dynamics (AIMD) simulations to explore the dynamical behaviors associated with the $\alpha-\beta$ transition of PVDF under various external stresses.

**METHODS**

**Prototype Routes for $\alpha-\beta$ Phase Transition of PVDF.**

Recently, Ranjan and his co-workers proposed a topological model of the transition route from the $\alpha$ phase to the $\beta$ phase and calculated the associated potential energy profiles with and without an external electric field.\(^{40}\) To determine the most energetically favorable transition pathway, one is required to examine the extremely vast potential energy surface associated with a large number of degrees of freedom, in principle, because the dynamics associated with the $\alpha-\beta$ conformational change involves complex torsional and rotational motions. However, following previous discussions,\(^{22-24}\) we considered the two most probable $\alpha-\beta$ phase transition paths of PVDF in the bulk phase under an external electric field and mechanical stretching in this study. We represent these proposed routes schematically in Figure 1. The first route (route I), which was named the electric-field-induced phase transition,\(^{22}\) was first proposed by Davis and co-workers. Route I starts with the transformation of the $\text{tg}^g\text{g}$ chain in the $\alpha$ phase to the polar $\delta$ phase by intramolecular rotation of CH$_2$ upward and CF$_3$ downward about the $g$ and $g'$ bonds, respectively, followed by conformational change from $\text{tg}^g\text{g}$ to an all-trans $\beta$ structure. Earlier experimental studies by Takahashi and his co-workers have revealed the existence of the $\delta$ phase.\(^{46-51}\) Both steps require external electric fields, and the second step requires a stronger electric field than the previous step.\(^{22}\) On the other hand, route II assumes that the mechanical stretching has a dominant role. Many experimental results have revealed that, even though the crystallinity of a sample is low after stretching, the content of the trans conformation is still quite high, and the polymer chains are well-aligned in the direction of stretching.\(^{23,24}\)

Figure 1. Two proposed transition routes from the $\alpha$ phase to the $\beta$ phase. Route I (upper): $\alpha$ → $\delta$ → $\beta$. Route II (lower): $\alpha$ → $\beta$(I) → $\beta$(II). The green arrows signify conformational changes caused by intramolecular rotations about the $g$ and $g'$ bonds, and the red arrow indicates rotation of the whole PVDF chain by 180°.

Two proposed transition routes from the $\alpha$ phase to the $\beta$ phase. Route I (upper): $\alpha$ → $\delta$ → $\beta$. Route II (lower): $\alpha$ → $\beta$(I) → $\beta$(II). The green arrows signify conformational changes caused by intramolecular rotations about the $g$ and $g'$ bonds, and the red arrow indicates rotation of the whole PVDF chain by 180°.

Because the $\alpha-\beta$ phase transition of PVDF accompanies the change of lattice structure, we used the G-SSNEB method to consider the deformation of the lattice structure as well as relaxation of the atomic configurations along the transition pathway.\(^{47}\) For the G-SSNEB calculations, we discretized the path connecting the initial and final configuration into 10 (for route I) and 9 (for route II) steps for each route, and the electronic energies and the conformations of the intermediate images generated by the NEB procedure were optimized by applying the aforementioned condition. The geometry optimizations of the respective images involved in each route were continued until the maximum total atomic force was smaller than $10^{-3}$ $\text{eV/Å}$. We also performed NVT AIMD simulations using the Nose thermostat at nonzero temperature to examine the transition behavior depending on simulation conditions, such as lattice parameters and initial configurations of the polymer chains.\(^{56}\) The NVT simulations were performed for 25 different simulation conditions at 600 K, a temperature slightly higher than the experimentally estimated ferroelectric Curie temperature of pure PVDF.\(^{5}\) Each simulation was performed for 5 ps, with a time step of 1 fs. The detailed descriptions for these 25 simulation conditions are presented in the Results and Discussion section with the discussions of the AIMD simulation results.

**RESULTS AND DISCUSSION**

**Two Transition Pathways and Stress Analysis.** We calculated the MEPs corresponding to the proposed transition routes I and II using the G-SSNEB method. The energy profile for each transition route is plotted in terms of the energy difference measured from the minimum energy state of the $\alpha$ structure in Figure 2. As a reaction coordinate, which can effectively represent the complex change in 3N-dimensional coordinate space, we introduced a simplified measure to quantify the advancement of the transition along the route. We defined the index of advancement, $Q_q$, as an accumulated distance from the initial state to the $i$th image, normalized by the sum of all distances between adjacent images

$$Q_q = \frac{\sum_{i=1}^{j-1} |\mathbf{q}_i + 1 - \mathbf{q}_i|}{\sum_{i=1}^{M-1} |\mathbf{q}_i + 1 - \mathbf{q}_i|}$$

(1)

where $\mathbf{q}_i = (r_{i1}, r_{i2}, ..., r_{in})^T$, $r_{ik}$ is the coordinate of the $k$th atom in the supercell of the $i$th image, $N$ is the total number of atoms...
in the supercell, and \( M \) is the total number of images on each transition route employed in the G-SSNEB calculations, including the initial and final images. The energy profile in Figure 2 indicates that route I looks slightly more favorable than route II at zero-field because the highest energy barrier in route I is lower than that of route II (53 meV/CH\(_2\)CF\(_2\) unit for route I compared with 70 meV/CH\(_2\)CF\(_2\) unit for route II). This is because image 5 contained in route II is in an energetically unstable \( \beta(I_1) \) phase. As seen from Figure 1, the CF\(_2\) groups belonging to each chain in the supercell become close to each other in image 5, and this configuration induces strong repulsive interchain Coulomb interaction between the CF\(_2\) groups. Both routes have three energy barriers. Variations of each of the 12 C–C–C–C dihedral angles, initially in gauche forms, along each transition route are shown in Figure 3. Route I (black solid line in Figures 2 and 3a) starts with a relatively low barrier (21 meV/CH\(_2\)CF\(_2\) unit), which accompanies a transformation from \( \alpha \) to a locally stable \( \delta \) phase. The second energy barrier representing the step that involves the change of backbone structure from the \( \delta \) phase to the \( \beta \) phase is split in two due to the cell deformation. The potential energy profile of route I shows a pattern similar to the one obtained by Ranjan et al.,\(^{40} \) except that the second energy barrier split in two and the barrier itself becomes significantly lowered due to (i) nonconcerted torsional motion of the carbon backbone and (ii) stabilization of the structure of the intermediate images by lattice relaxations. In the case of route II (red solid line in Figures 2 and 3b), the first two energy barriers are due to the transformation of the backbone structure from \( tgtg' \) to all-trans to form the \( \beta(I_1) \) phase. From the \( \beta(I_1) \) phase, transformation to the \( \beta(I_0) \) phase is achieved by overcoming a small potential energy barrier, as indicated at the eighth image. This small barrier arises from the global rotation of each chain, and thus, all of the local dihedral angles belonging to the same chain are nearly fixed during the rotation (see Figure 3b).

Deformation of the lattice as the \( \alpha-\beta \) phase transition proceeds along the transition routes induces a further noticeable stabilization energy for each image, which cannot be obtained in simulations with fixed lattice structure or in single-chain simulations.\(^{3,40} \)

Parts a and b of Figure 4 show variations of the interchain configuration between the two PVDF chains in a supercell for routes I and II, respectively. In the case of route I, lattice deformation by shear mode is negligible during the \( \alpha \) to \( \delta \) transition, and the CH\(_2\) (CF\(_2\)) group in one chain and the CF\(_2\) (CH\(_3\)) group in the neighboring chain maintain the closest pairing during the transition. On the other hand, noticeable shear deformation of the lattice structure occurs during the \( \delta \) to \( \beta \) transition (see Figure 4b). During this transition, CH\(_2\) (CF\(_2\)) groups in one chain form the closest pairing with the same CH\(_2\) (CF\(_2\)) group of the neighboring chain due to the shear deformation. On the other hand, in the case of route II, shear deformation of the lattice structure occurs both in \( \alpha \) to \( \beta(I_1) \)
and in $\beta(I_a) \rightarrow \beta(I_c)$ transitions (see Figure 6b). If we imposed
the orthogonality condition on the lattice structure during the
transition from $\beta(I_a)$ to $\beta(I_c)$, the aforementioned change of
carbon pairing would occur only by longitudinal sliding of
the chain, which would be the energetically much more unfavorable
one. For example, if the $\beta(I_a) \rightarrow \beta(I_c)$ transition occurred
without shear deformation of the lattice structure, the potential
energy barrier with a 100 meV/CH$_2$CF$_2$ unit would be
noticed.

Next, we analyzed the electronic enthalpy change of the $\alpha \rightarrow \beta$
phase transition of PVDF under the external electric fields. On
the basis of the transition pathways we obtained, simple estimation
of the effects of an external electric field on the energy profiles of the
transition pathways is possible. When an external field $\mathbf{E}$ is applied, the enthalpy of the system is
modified by the amount $-VE$, where $P$ and $V$ are the
macroscopic polarization and cell volume, respectively. The
macroscopic polarization was obtained by use of the Berry-
phase method. The behavior of the macroscopic polarization
as the $\alpha \rightarrow \beta$ transition proceeds along each transition route is
shown in the inset of Figure 2. The variations of the enthalpy
curves under various external electric fields are also shown in
Figure 2 as dashed lines. For route I, the first barrier is not
altered by the electric field due to the almost nonpolar first
image. On the other hand, the enthalpy for the second barrier is
significantly lowered. However, because the polar $\delta$ phase is
also stabilized, the net height of the second energy barrier does
not change much under the external electric field. For route II,
the change of dihedral angles occurs in a nonpolar state.
Therefore, the energy barrier is not altered by the electric field
until the system reaches the $\beta$ (I$_c$) phase (image 5). On the
other hand, the images located after the $\beta$ (I$_c$) phase show
noticeable stabilization under the external electric field.

From the potential energy curve and change of the
conformational structure of every image along each route, we
estimated the minimum magnitude of stress accompanied by
transforming the $(i-1)$th to the $i$th image. Analysis of the
behaviors of the stress accompanied by transforming the $(i-1)$th to the $i$th image should provide an understanding of the
$\alpha \rightarrow \beta$ transition mechanism and also useful information
regarding how to improve the ferroelectric property of the $\beta$
structure of the PVDF. Because we allowed the change of all
lattice parameters and lattice angles in computing the transition
routes, the lattice structure of each image is a naturally non-
orthorhombic structure. Therefore, the strains have to be
projected onto the three basis vectors consisting of the lattice of
the $i$th image, rather than onto the Cartesian laboratory frame
($\hat{x}$, $\hat{y}$, and $\hat{z}$). Then, the stress can be estimated as follows. Our
calculations are based on the assumption that the structures of
the $(i-1)$th and $i$th images are connected in such a manner
that the $i$th image is reached from the $(i-1)$th image by linear
deformation. This approximation should be valid if the
deformation from the $(i-1)$th to the $i$th image is small.
Thus, it may not work well for some images, especially from
the fifth to the sixth (route I) and the fourth to the fifth (route II),
where the structural change between the two images becomes
large. Still, our estimations under this approximation seem to
provide reasonable and important results. With this assumption,
the following relation holds between the deformation tensor $F$
and $h$, which is a matrix composed of three lattice vectors $\vec{i}$, $\vec{j}$,
and $\vec{\ell}$ of the $i$th image

$$F = h h^{-1}.$$  \hspace{1cm} (2)

Then, the symmetric strain tensor $\epsilon$ is written as

$$\epsilon = \begin{bmatrix} \epsilon_{xx} & \epsilon_{xy} & \epsilon_{xz} \\ \epsilon_{yx} & \epsilon_{yy} & \epsilon_{yz} \\ \epsilon_{zx} & \epsilon_{zy} & \epsilon_{zz} \end{bmatrix} = \begin{bmatrix} \epsilon_1 & \epsilon_2 & \epsilon_3 \\ \epsilon_2 & \epsilon_4 & \epsilon_5 \\ \epsilon_3 & \epsilon_5 & \epsilon_6 \end{bmatrix} = \frac{1}{2}(U + U^T)$$ \hspace{1cm} (3)

where $U = F - I$ is displacement tensor. In this equation, the
numeric indices for strain tensor elements obey the Voigt

![Figure 5. Estimation of the stresses accompanied by transforming the $(i-1)$th image to the $i$th image along each transition route. The plots in parts a and b present variations of the three axial stresses for routes I and II, respectively. Black, red, and green curves indicate $\sigma_1$, $\sigma_2$, and $\sigma_3$, respectively. Parts c and d show the three shear stress curves for routes I and II, respectively, and the black, red, and green curves indicate $\sigma_4$, $\sigma_5$, and $\sigma_6$.](image-url)
notation (1, 2, 3, 4, 5, and 6, corresponding to \(aa, bb, cc, bc, ca,\) and \(ab\), respectively). Here, the components \(\epsilon_{\alpha\beta}\) and \(\epsilon_{\beta\gamma}\) represent the axial strain along the lattice vectors \(\vec{a}, \vec{b},\) and \(\vec{c}\) of the \(i\)th image, and the components \(\epsilon_{\alpha\gamma}, \epsilon_{\beta\alpha}\) and \(\epsilon_{\gamma\beta}\) represent the shear strain between \(\vec{b}\) and \(\vec{c}\), \(\vec{c}\) and \(\vec{a}\), and \(\vec{a}\) and \(\vec{b}\) of the \(i\)th image, respectively. Then, the stress tensor \(\sigma\) can be written as

\[
\sigma = C \epsilon; \quad \sigma_{\alpha\beta} = \sum_{\beta} C_{\alpha\beta\alpha\beta} \epsilon_{\alpha\beta}
\]

(4)

where \(C\) is a \(6 \times 6\) elastic stiffness constant matrix and \(\sigma\) and \(\epsilon\) are in the form of column vectors (for example, \(\epsilon = (\epsilon_{1}, \epsilon_{2}, \epsilon_{3}, \epsilon_{4}, \epsilon_{5}, \epsilon_{6})^T\)). Similar to the case with the strain tensor, we can denote the components \(\sigma_{11}, \sigma_{22},\) and \(\sigma_{33}\) as axial stress and the components \(\sigma_{12}, \sigma_{23},\) and \(\sigma_{31}\) as the shear stress between \(\vec{b}\) and \(\vec{c}\), \(\vec{c}\) and \(\vec{a}\), and \(\vec{a}\) and \(\vec{b}\) of the \(i\)th image, respectively. Calculation of the stress tensor using the above equation requires information about \(C_{\alpha\beta}\) for PVDF. For that, we calculated the elastic stiffness matrix for the stable \(\alpha\) and \(\beta\) structures and used those values. For the images from 1 to 8 in route I and the images from 1 to 5 in route II, whose structures are similar to the \(\alpha\) structure, we borrowed the \(C_{\alpha\beta}\) of the \(\alpha\) structure. For the images from 9 to 10 in route I and the images from 6 to 9 in route II, whose structures are similar to the \(\beta\) structure, we used the \(C_{\alpha\beta}\) of the \(\beta\) structure. The values of each element of \(C\) are in good agreement with the results of Pei and Zeng.39

In Figure 5, the behaviors of stress tensors for axial stresses parallel to the \(a, b,\) and \(c\) directions (Figure 5a and b) and for shear stresses (Figure 5c and d) are presented as functions of \(Q\) for each transition route. Additionally, Figure 6 shows the behaviors of lattice parameters and angles (\(a, b,\) and \(c\) in Figure 6a and \(\alpha, \beta,\) and \(\gamma\) in Figure 6b) for each transition route. The characteristic feature of the stress common for both routes is the large and positive value of \(\sigma_{11}\), which represents the axial stress parallel to the chain direction and is responsible for the conformational change from \(tgg'\) to \(all-trans\). The maximum values of \(\sigma_{11}\) of route I (10.46 GPa) and route II (8.84 GPa) are nearly the same as each other, taking into account the approximation employed in the estimation of \(\sigma_{11}\). From the observation of stabilization of the electronic enthalpy by the electric field, together with the behavior of the axial stress along the chain direction, we can deduce the following possible scenarios for the \(\alpha-\beta\) transition: (1) Under an electric field, route I is favorable due to larger field-induced stabilization of enthalpy than route II. (2) On the other hand, route II can be more favorable when mechanical drawing is applied. A few decades ago, Davis et al. showed by experimentation that the transition from the \(\alpha\) phase to the \(\beta\) (\(I_p\)) phase, which is consistent with route I, is only possible by external electric field.23 According to their study, a stronger electric field makes it possible to transform the \(\beta\) phase to the \(\beta\) (\(I_p\)) phase. Consistent with the second scenario, the transformation to the \(\beta\) (\(I_p\)) phase was experimentally realized by Sencadas et al. and Gomes et al.23,24 Their experimental results revealed that the fraction of \(trans\) form increases by mechanical drawing. However, the crystallinity of the PVDF thin film is still low, which implies that the transformation from the \(\beta\) (\(I_p\)) phase to the \(\beta\) (\(I_p\)) phase cannot be achieved efficiently by mechanical drawing only. We observed in Figure 5a and b that \(\sigma_{11}\) becomes negative when \(tg\) transforms to an \(all-trans\) structure (between image 6 and 7 in route I and between image 2 and 3 in route II) for both transition routes. Additionally, during this structural transformation, we observed comparatively large shear deformations, even though magnitudes of the shear stresses are very small. This is due to the small elastic coefficients \(C_{44}, C_{55},\) and \(C_{66}\). On the other hand, the behaviors of shear deformations between the two routes show a noticeable discrepancy. In the case of route I, large changes in cell angles \(\alpha\) and \(\beta\) imply that the shear deformations are mainly in the planes parallel to the chain direction. This is due to the change of chain stacking between the two chains, leading them to form the closest pairing CH\(_2\) (CF\(_2\)) groups in one chain with the CH\(_2\) (CF\(_2\)) group of the neighboring chain (see Figure 4a). In the case of route II, large changes in \(\alpha\) and \(\gamma\) were observed. The change in \(\alpha\) is based on the same grounds as the case of route I. On the other hand, unlike the case of route I, the large distortion of \(\gamma\), which represents the shear deformation in the plane perpendicular to the chain direction, is observed in the transition from \(\alpha\) to \(\beta\) (\(I_p\)), as well as from \(\beta\) (\(I_p\)) to \(\beta\) (\(I_p\)). The Coulomb repulsion between the CF\(_2\) groups belonging to the neighboring chains is strongest if the two chains are in the antiparallel configuration maintaining the orthorombic structure, and this Coulomb repulsion is substantially reduced by the change in \(\gamma\). The shear deformation caused by a change in \(\gamma\) has been predicted by Takahashi et al.38

One interesting feature to note is that, if we compare the variations of the cell parameters in the \(a\) and \(b\) directions, the change in the \(a\) direction is noticeably larger than that in the \(b\) direction, even though the magnitudes of the axial stress in the \(a\) and \(b\) directions along each transition route are all nearly same. This implies that, when the isotropic stress (such as hydrostatic pressure) is applied to the bulk PVDF system, a change of the interchain distance in the \(a\) direction should be far larger than the change of distance in the \(b\) direction.39,40

We will have further discussions about this property in relation.
to the transition behavior from the \( \beta (I_p) \) phase to the \( \beta (I_\alpha) \) phase using the AIMD simulation results performed under various simulation conditions in the next section.

**Ab Initio Molecular Dynamics Simulations at Nonzero Temperature.** We performed the AIMD simulations using the Nosé thermostat for all possible combinations of the cell parameters and the initial orientations presented in Table 1, Table 1. Simulation Conditions Employed in the AIMD Simulations

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<th>III</th>
<th>IV</th>
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<table>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<td>-0.81</td>
<td>-0.50</td>
<td>-0.20</td>
<td>0.03</td>
</tr>
<tr>
<td>( (\theta_\alpha - \theta_\beta)^{f} )</td>
<td>(180)</td>
<td>(144)</td>
<td>(120)</td>
<td>(102)</td>
<td>(88)</td>
</tr>
</tbody>
</table>

"The simulation codes are expressed in two different ways. The first code, expressed in Roman numerals (I, II, III, IV, and V), represents the lattice parameter \( a \) (in Å units) of the supercell under which the simulations are performed. The second code, expressed in capital letters (A, B, C, D, and E), represents the initial configurations employed in the simulations. The specifications of the initial configurations are elucidated in the footnote. Additionally, the relative initial orientations between the two chains in the supercell are represented both by cosine values and by angles (see eq 5)." For the AIMD simulation, specification of the initial coordinates and velocities of every site atom in the supercell is necessary. This structural information was obtained at an atomistic level: in the case of condition I, it was obtained from the \( \alpha \) structure in its minimum energy conformation, and in the case of conditions B, C, D, and E, it was obtained from the structure at several specified times in the simulation trajectory performed under condition II-A. (see footnote d). The \( a \) value of condition III was taken from the lattice of the minimum energy state of the \( \beta \) phase. \( \alpha \) The initial structures represented as B, C, D, and E are the structures taken at each instant of 501, 684, 877, and 1004 fs during the AIMD simulation performed under condition II-A. The values in the parentheses are relative angles between two chains in the supercell expressed in units of degrees.

and we observed the structural changes of the PVDF chain for 5 ps. Throughout all of the AIMD simulations, the temperature was fixed at 600 K. As seen in Table 1, the cell parameter condition from I to V is distinguished into the magnitude of the parameter \( a \). The values of the \( a \) parameter listed in Table 1 are in descending order from I to V; i.e., the interchain distance in the \( \alpha \) direction decreases from I to V. Figure 7a shows time-dependent profiles of the mean dihedral angle for a total of 24 dihedral angles for the five different \( a \) values. In these simulations, \( b \) and \( c \) are fixed to the lattice parameter value corresponding to those of the stable \( \beta \) phase, and the initial states of the PVDF chains were taken from the conformation of the stable \( \alpha \) phase. We can see clearly that the mean dihedral angle is rapidly transformed to that of all-trans chains for all five simulations within approximately 1 ps. In Figure 7b, time-dependent profiles of individual dihedral angles, initially in gauche form, are presented. We can see that the time-dependent behaviors of the dihedral angles under condition IV-A are similar to the behavior of the dihedral angles along route II (Figure 3b). Because the cell parameter \( c \) of condition IV is set as the same as that of the stable \( \beta \) structure, it implies that the phase transition of PVDF from \( \alpha \) to \( \beta \) prefers route II if the mechanical drawing is applied. The conformational changes from tgtg' to the all-trans form do not occur simultaneously; i.e., the transition is a nonconcerted one, as shown in the G-SSNEB simulations. We also observed that dynamical patterns of the dihedral angles for four other simulations (simulations under I-B, -C, -D, and -E) are similar to the one shown under condition I-A. On the basis of the time-dependent behavior of these dihedral angles, we can further deduce that, when mechanical drawing is applied to the PVDF system, formation of the \( \beta \) phase is initiated at two or three monomer units, and it propagates to neighboring units. Such a mechanism is supported by recent experiments by Li and co-workers, who showed that, under mechanical stretching, the \( \beta \) phase initially emerges in the middle of a spherulite of the \( \alpha \) phase, and then the region of the \( \beta \) phase expands as the transition proceeds. Both parts a and b of Figure 7 show that mechanical stretching acting parallel to the chain direction readily transforms the PVDF chain into the all-trans form. However, only with the dihedral angle, one cannot distinguish the relative orientation between the two chains determining the polarity of the system. To take this into account and to determine whether the PVDF system is in the \( \beta (I_p) \) phase or the \( \beta (I_\alpha) \) phase (which is an important criterion reflecting its crystallinity), we further introduced a parameter \( K \), which measures the relative orientation between the two PVDF chains in the supercell. The cosine angle between the orientation of the two polymer chains is defined as

\[
K = \frac{1}{N_{\text{CH}_2}} \left( \sum_{\text{CH}_2 \in I} \mathbf{r}_{\text{C} - \text{H}} + \sum_{\text{CH}_2 \in I} \mathbf{r}_{\text{C} - \text{C}} \right) \]

(5)
and \(N_{\text{C},i}^{(I)}(I = A, B)\) denotes the total number of carbons in the \(i^{th}\) chain. The first term on the RHS is the sum of the \(C\)–\(H\) bond vector that directs from C to H for all CH2 groups in the \(i^{th}\) chain, and the second term is the sum of the \(C\)–\(F\) bond vector for all CF2 groups that directs from F to C in the \(i^{th}\) chain. Therefore, by definition, two chains are in a completely nonpolar state when \(K = -1\) and in a maximum polar state when \(K = +1\). Figure 8 shows the time-dependent behavior of

![Figure 8](image)

Figure 8. Time-dependent behavior of the cosine value of the angle between the two chains (see eq 5) obtained from the AIMD simulations for the five different \(a\) values listed in Table 1. The initial state was set as the \(\alpha\) phase in its minimum energy conformation for all five simulations. Transitions from the \(\beta\) \((I_a)\) structure to the \(\beta\) \((I_p)\) structure were only allowed for \(a = 11.95, 9.96, \) and 8.79 Å.

The relative orientation between the two chains for five different \(a\) parameters. The simulation under condition V-A, which has the smallest \(a\), shows that the configuration of the two PVDF chains can hardly escape out of the \(\beta\) \((I_p)\) phase. On the other hand, the simulations under conditions I-A, III-A, and IV-A, which have larger values of \(a\) than V-A, show that the two chains are transformed to a polar configuration and remain in the polar configuration even though noticeable fluctuations are present in the relative orientation \((0 < K < +1)\). However, the simulation under condition II-A shows only heavy oscillation of the relative orientation within the antiparallel phase \((-1 < K < 0)\). The simulation results imply that lattice parameter \(a\) can play an important role in transforming the chains into a parallel configuration. However, the simulation results in Figure 8 do not show consistent behavior with respect to the magnitude of \(a\). Simulation under condition III-A, whose value of \(a\) is between those of I-A and III-A, does not show a transform to the parallel configuration. In the case of V-A, it is thought that the size of \(a\) is too small and the compression effect is too strong to allow chain rotation. Because the \(a\) in condition II-A is larger than that in III-A, it is reasonable to expect the \(\beta\) \((I_p)\) form under II-A. Therefore, the reason that the simulations under II-A do not result in the \(\beta\) \((I_p)\) form must be rooted in different ground. In principle, to obtain a statistically quantitative answer for how readily the two chains can transform to a parallel configuration, simulations under fixed same-cell parameters are necessary, but with a large number of sets of different positions and velocities for every site atom assigned from a canonical ensemble of velocity distributions. This requires extremely heavy computational work. Still, with a limited number of simulation studies, we are able to have a qualitative understanding of the role of the simulation condition for the transition from \(\beta\) \((I_p)\) to \(\beta\) \((I_a)\).

We have performed a total of 25 AIMD simulations under all combinations of the five cell parameters and the five initial configurations listed in Table 1, and we plotted five sets of diagrams in Figure 9, which show how the relative initial orientations between the two chains change depending on the initial configurations at a given cell parameter condition. Thus, we observed the feasibility of the transition from \(\beta\) \((I_p)\) to \(\beta\) \((I_a)\). We chose the initial configurations A, B, C, D, and E, as indicated in the footnote of Table 1 (see d and e). On the other hand, the initial velocities of each site atom were assigned according to the rule of the canonical distribution.

To examine the initial-condition-dependent time profiles of the relative orientation, the cosine values were plotted in Figure 9 with respect to the initial configurations ranging from A to E at each respective cell parameter condition. Figure 9a shows that, if the interchain distance in the \(a\) direction is too large, the transition to \(\beta\) \((I_p)\) depends strongly on the initial condition specified as initial positions and velocities assigned for each site atom. The simulations under conditions I-A and I-C show transformation to the \(\beta\) \((I_p)\) phase, whereas other cases do not. The simulations under the cell parameter conditions II and III show similar patterns, but the rates of transition to the \(\beta\) \((I_p)\) phase are even worse. On the other hand, we notice that whole series of simulations resulted in the \(\beta\) \((I_p)\) form under cell parameter condition IV. Finally, for the series of simulations under condition V, which has the smallest value of \(a\), two out of five cases resulted in \(\beta\) \((I_p)\). From observation of the series of simulation results, we can deduce the following remark regarding the role of cell parameter conditions, which can be controlled by external stress, in the \(\alpha\)–\(\beta\) transition. It is clear that stretching along the \(c\) direction is essential for transformation of PVDF chains to the all-trans structure. However, mechanical stretching parallel to the \(c\) direction by itself is not sufficient. Simultaneous application of appropriate amounts of compression along the \(a\) direction is necessary to obtain a high-quality ferroelectric \(\beta\) \((I_p)\) phase. If either the compression effect is too large or too small, whether the chain rotation resulting in the \(\beta\) \((I_p)\) configuration is allowed or not depends sensitively on the initial condition, i.e., the atomic positions and velocities. However, assigning such an appropriate initial condition is not possible in the manufacturing process. On the other hand, squeezing in the \(a\) direction can be realized by experimental methods. The stress curve shows that isotropic compression (such as hydrostatic pressure) induces a confinement effect mainly along the \(a\) direction because the change of the supercell length in the \(a\) direction is much larger than that of \(b\), even though the magnitude of axial stress along \(a\) and \(b\) is similar. This means that, when isotropic compression is applied, it is mainly the interchain distance in the \(a\) direction that changes (see Figures 5 and 6). The conclusion that we deduced from our simulation results is consistent with the experimental result obtained by Matsushige and his co-workers, in which they studied the role of external pressure and observed enhancement of the \(\beta\) \((I_p)\) phase under external hydrostatic pressure, and also with the experimental study by Cauda et al., which showed enhancement of ferroelectricity of the \(\beta\) phase after employing the nanoconfinement technique by using a porous alumina membrane.

**CONCLUSION**

In summary, we proposed two independent transition routes that connect the nonpolar \(\alpha\) phase with the polar \(\beta\) phase of PVDF in the bulk phase with the assistance of the G-SSNEB method. We also presented the modified potential energy curves under the electric field by estimating the electric enthalpy depending on the strength of the electric field, and we computed the stresses along the transition route. Between the
two transition routes, route I, which is named the electric-field-induced transition route, starts with the transition from the $\alpha$ phase to the $\delta$ phase. The $\alpha$ form is a nonpolar phase, and the $\delta$ form is a polar phase. This transition accompanies the intramolecular rotation of CH$_2$ upward and CF$_2$ downward about the $g$ and $g'$ bonds, respectively, and the external electric field is essential for this transition. The next step of the transition is from $\delta$ to $\beta$ ($I_p$), which involves changing the backbone structure from tgtg' to the all-trans form. It is well-known that this step requires a stronger external electric field.

On the other hand, route II directly starts with a transition from tgtg' to the all-trans form, which is mostly an antiferroelectric phase $\beta$ ($I_a$). Because this transition involves the change of backbone structure from tgtg' to the all-trans form, mechanical drawing is essential for this step. The next step is the transition from $\beta$ ($I_a$) to $\beta$ ($I_p$) form by chain rotation. Route I is consistent with the generally known manufacturing process to obtain the $\beta$ ($I_p$) phase of bulk PVDF, which is summarized as an application of the electric field to transform $\alpha$ to $\delta$, followed by application of stronger electric fields to transform $\delta$ to $\beta$ ($I_p$).

Our proposed route II, together with the series of AIMD simulation studies, suggests that an alternative manufacturing process can be possible, i.e., the combination of mechanical stretching parallel to the $c$ direction and application of an adequate amount of squeeze parallel to the $a$ direction at the same time. The squeeze in the $a$ direction can be experimentally realized by simply employing hydrostatic pressure because our stress curve analysis shows that an isotropic compressive force mainly changes cell parameter $a$, whereas changes in other cell parameters are negligible. Our theoretical analysis based on the AIMD simulations is consistent with current experimental studies.

### AUTHOR INFORMATION

#### Corresponding Author

*E-mail: eklee@kaist.ac.kr.

#### Notes

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