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Computer simulation of structure and ferroelectric phase transition of vinylidene fluoride copolymers

Part 3. The motion of molecular chains in the ferroelectric phase transition

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Abstract

Molecular chain motions in the ferroelectric phase transition of vinylidene fluoride (VDF)–trifluoroethylene (TrFE) copolymers have been studied by using molecular dynamics (MD) technique. The MD calculation was made for the crystal structures of VDF 50 and 70 mol% copolymers. In the ferroelectric phase or the low temperature phase, the parallel arrangement of the CF_2 dipoles of the zigzag chains were found to be the energetically stable packing structure of the chains. The slightly deflected *trans*-zigzag chains were found to librate with relatively large amplitudes around their chain axes. In the non-polar paraelectric phase or the high temperature phase above the phase transition temperature, the molecular chains were found to take the statistically-disordered conformations of TG and T_3G. The molecular motion became very vigorous by coupling of the rotational motion with the exchange motion between the *trans* and *gauche* conformations. These simulations were found to be consistent with the experimental data of solid-state NMR, IR, Raman, and X-ray diffraction. The transition temperatures calculated for VDF 50 and 70 mol% copolymers were about 425 and 480 K, respectively, corresponding relatively well to the experimental data. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Vinylidene fluoride copolymer; Ferroelectric phase transition; Molecular motion

1. Introduction

Poly(vinylidene fluoride) (PVDF) and vinylidene fluoride (VDF) copolymers with trifluoroethylene (TrFE) or tetrafluoroethylene (TFE) are the first synthetic polymers exhibiting the ferroelectric phase transition phenomenon. In order to relate the physical property changes observed in this phase transition with the structural changes in the crystals, many kinds of measurement have been performed such as X-ray diffraction, infrared spectra, Raman spectra, neutron scattering, electron diffraction, NMR spectra and thermal analysis [1–6]. It has been found out that the three crystalline forms, the low temperature (LT) phase, the high temperature (HT) phase, and the cooled (CL) phase, participate in the ferroelectric phase transition [3–5]. In the LT phase the all-*trans* zigzag chains are packed regularly with their CF_2 electric dipoles oriented in parallel along the *b* axis. In the HT phase, the chain conformations are built by the statistically random arrangements of TG, TG^-, T_3G, and T_3G^-. The CL phase is proposed to take a kind of irregular structure constructed by a disordered packing of *trans*-zigzag chain segments connected by *gauche* bonds.

The common and most important structural feature in the phase transition of VDF–TrFE copolymers is the chain conformational change which occurs drastically between the all-*trans* zigzag form and the conformationally-disordered form [7]. Besides, the molecular chains rotate around the chain axis in the HT phase. We may speculate easily that the rotational motion is coupled with the *trans*–*gauche* conformational changes, although the details have not yet been clarified experimentally well. Several papers were reported about the theoretical interpretation of the structural change in this phase transition [4,8–11]. But such a complicated motion of the chains could not be taken into consideration in the calculations. In the previous papers [12,13], we tried to simulate the phase transition of VDF–TrFE copolymers on the basis of the molecular dynamics (MD) method and obtained the information on the chain conformation change and the molecular motion in the course of the phase transition. We believe this MD calculation was the first success in the computer simulation of the complicated structural changes in the crystal lattice of VDF–TrFE

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copolymers. In order to extract the essential factors governing the transitional behavior of this polymer system, we need to analyze the MD calculation results in more detail. In the present paper, by focusing our attention on the coupling motion of the chains, the detailed analysis will be made to know the key points of this characteristic phase transition.

2. Simulation method

2.1. Force field

The force field parameters published in the previous paper [13] were used in the present MD simulation. The MD calculation was carried out by using a commercially available software (POLYGRAF, version 3.21, Molecular Simulations Inc.). The non-bonded interatomic interaction energies such as Coulombic interaction energy and van der Waals $1/R^6$ interaction energy were calculated by the ABCA Ewald procedure [14]. Repulsive van der Waals interaction energy was calculated within 7.6 Å. The total potential energy was calculated by summing the energies of the bond stretching, angle bending, torsional potential, and their cross terms [13].

2.2. Construction of models

In the present paper the VDF contents were assumed to be 50 and 70 mol%. Three types of the MD cells were constructed. According to the NMR analysis [15], VDF–TrFE copolymers are random as for the monomer sequences of VDF and TrFE units in the molecular chains. In the case of VDF 50 mol% model, the type I model, for example, was constructed by packing the 16 chains which consisted of random sequences of five VDF and five TrFE monomer units. The positions of molecular chains in the lattice were determined by a random number. The tacticity of TrFE monomers was assumed to be atactic. The monomer sequences of the chains in the MD cells were determined independently. Three-dimensional periodic boundary condition was charged for the MD unit cell. Therefore, the chains were connected infinitely along the direction of the *c* axis. As to the direction of the chains along the *c* axis, the following several models were constructed. 8u16 model: the eight chains were packed downwards and the other chains were upwards along the *c* axis, where the upward direction was defined in such a way that the direction vector of CH_2CF_2 unit pointed into the positive direction of the chain axis. model u: all the chains were set upwards. The cell of type II contained longer molecular chains, each of which consisted of random sequences of ten VDF and ten TrFE monomers in each chain. The type III cell was constructed by packing larger number of chains, 36 chains consisted of random sequences of five VDF and five TrFE monomers in each chain. The type II and III models were made only for VDF 50 mol% model.

Table 1
Axial lengths of the unit cells of the various models attained the equiliblium state at 300 K

Model	*a* (Å)	*b* (Å)	*c* (Å)
PVDF form I	9.05	4.93	2.59
VDF50-u	9.47	5.31	2.62
VDF50-8u16	9.43	5.34	2.62
VDF50u (36 chains)	9.56	5.27	2.62
VDF50u (20 mers)	9.54	5.32	2.61
VDF70-u (1)	9.40	5.16	2.61
VDF70-8u16 (1)	9.39	5.18	2.61
VDF70-u (2)	9.35	5.18	2.61
VDF70-8u16 (2)	9.28	5.18	2.61

2.3. Molecular dynamics calculation

MD calculations were performed based on the Parrinello–Rahman method [16] of the constant pressure and temperature with the Nose–Hoover thermostat [17,18] at the various temperatures such as 300 and 350 K. The calculation of the NPT ensemble was performed for about 20 ps. The simulation time was elongated or shortened by judging whether the state of the system was equilibrated or not. The MD cell parameters of VDF–TrFE copolymer systems attained the equilibrium state at 300 K are listed in Table 1.

3. Results and discussion

3.1. Comparison of the phase transitional behavior between VDF 50 and 70 mol% models

In the ferroelectric phase transition of VDF–TrFE copolymers, the electric polarization of the cell is an important index of the structure change in the cell. The dipole moment of each chain was calculated by the following equation

$$\vec{\mu}_k = \sum_j Q_j(k)\cdot\vec{X}_j(k) \tag{1}$$

where $Q_j(k)$ and $\vec{X}_j(k)$ were the electric charge and Cartesian coordinate vector of atom j belonging to the k‘th chain, respectively. The total polarization $\vec{P}$ of this model system was calculated by the following equation

$$\vec{P} = \sum_{k=1}^{N} \vec{\mu}_k / V \tag{2}$$

where N is the total number of the chains in the MD cell and V is the cell volume. The temperature dependence of the *b*-axis component (Ps-b) of the calculated electric polarization of the cell is shown in Fig. 1 for VDF 50-u, VDF 50-8u16, VDF 70-u, and VDF 70-8u16 models. The initial value of the calculated Ps-b was 8.5×10^{-2} C/m^2 for VDF 50 mol% models. Experimentally, the observed polarization corresponds mainly to the *b*-axis component, because the highly-poled samples were used where the crystal *b*-axis or the polar axis were highly oriented along the normal to

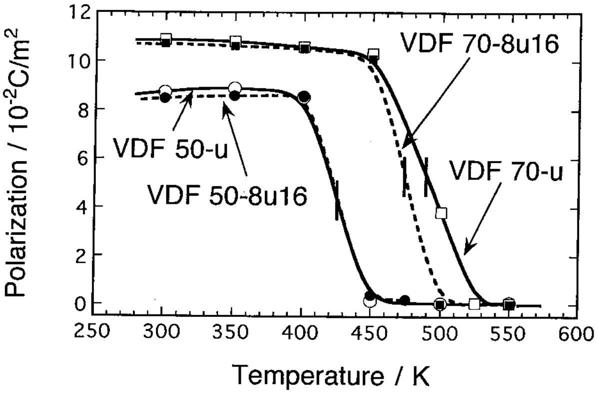
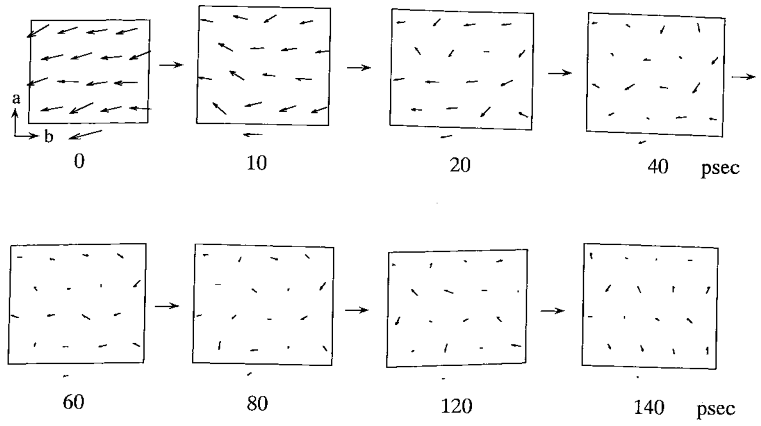


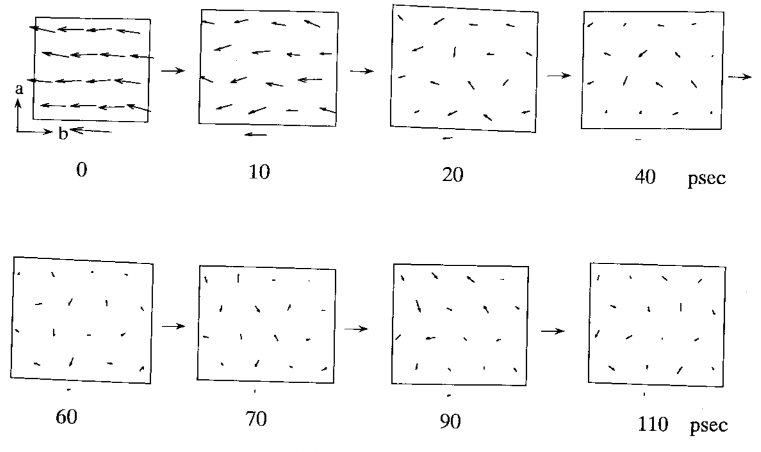
Fig. 1. Temperature dependence of electric polarizations (the *b*-axial component) calculated for VDF 50 and 70% -TrFE copolymers (u and 8u/16 models).

film surfaces. The permanent polarization actually observed for the poled VDF(52)–TrFE copolymer sample was 6×10^{-2} C/m^2 [2]. If the degree of crystallinity 0.7 is assumed for the bulk sample, then the polarization of the crystal lattice might be 8.6×10^{-2} C/m^2. The calculated values are in good agreement with the observed value. As the temperature rises, Ps-b becomes gradually small and decreases drastically around 420 K for VDF 50 mol% models, around 480 K for VDF 70 mol% models. The calculated Ps-b reached zero at higher temperature in both the cases of the VDF 50 and VDF 70 mol% models.

The time dependence of the dipole moments of the chains of VDF 50 mol% and VDF 70 mol% models (u models) in the phase transition temperature region are shown in Fig. 2 where the dipoles are projected on the plane perpendicular to the chain axis. In the case of VDF 50-u model at 450 K, the dipole moments of all the chains at 0 ps are almost equal in magnitude and are oriented in parallel along the *b* axis. After starting the MD calculation, the direction of each dipole moment was kept unchanged at the initial stage, but, as the cell volume expanded gradually, the magnitude of the dipoles became smaller because of the appearance of *gauche* (G^+ or G^-) conformation in the molecular chains. After that, around 20 ps, the dipole moments of several molecular chains were observed to change the orientation direction largely and fluctuate around the chain axis. In the equilibrated stage or after the passage of long time, the



(a) VDF 50-u



(b) VDF 70-u

Fig. 2. Time dependence of the motion of dipole moments of the (a) VDF 50 and (b) 70%-TrFE copolymer chains viewed along the chain axis (u models). An arrow shown at the bottom of each figure indicates the total polarization viewed along the chain axis.

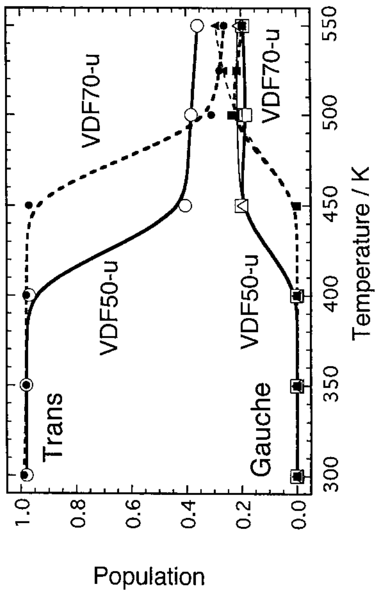


Fig. 3. Temperature dependence of the population of the *trans* and *gauche* conformations calculated for VDF 50 and 70%-TrFE copolymers (u models). ○: *Trans*; △: *Gauche* + ; and ▲: *Gauche* − .

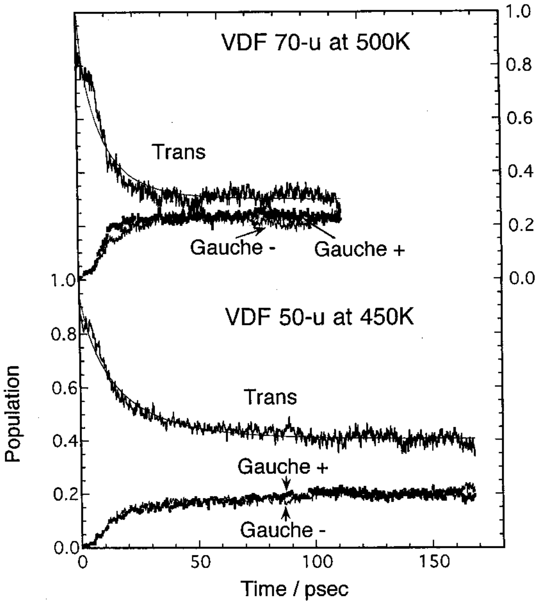


Fig. 4. Time dependence of the population of *trans* and *gauche* conformation fractions calculated for VDF 50 and 70%-TrFE copolymer (u models) at the phase transition temperatures.

dipole moments of the chains were negligibly small and the directions changed randomly because the chains rotated randomly around the chain axis.

In the case of VDF 70-u model, the temperature of inducing the conformational changes is about 50 K higher than that of the VDF 50-u model, although the behavior of the dipole moments is very similar. That is to say, the essential feature of the transition is almost common to both the VDF 50 and 70% copolymers, as already found in the experimental results [1].

The obvious difference between VDF 50-u and 70-u models was found in the ratio of *trans* and *gauche* contents in the backbone chains as stated in the previous paper [13]. In Fig. 3 is shown the temperature dependence of the population of the *trans* and *gauche* bonds of the skeletal chains of VDF 50-u and 70-u models attained the equilibrated state, where the *trans* and *gauche* angles were assumed to cover the torsional angles in the range of 150–210° (T), 30–90° (G^+), and 270–330° (G^-). The ratio of T was almost unity in the low temperature region and decreased drastically above the phase transitional temperature. In Fig. 4 is shown the time dependence of the population of T and G bonds at the phase transitional temperature. The ratio of T was unity at 0 ps and it decreased steeply and the ratio of the G^+ and G^- increased at the same time. At the equilibrated stage, the ratio of the T, G^+ and G^- is 40:20:20 for VDF 50-u model and 35:25:25 for VDF 70-u model. The *gauche* content in the HT phase is higher for the copolymer with higher VDF content. This tendency is consistent with the result observed by the Raman spectral measurement [19].

In the present MD calculation the temperature was raised suddenly from 0 K to the predetermined value, 450 K for VDF 50-u or 500 K for VDF 70-u. We calculated the decay curves of the population of T conformation in this process of temperature jump and fitted the curves by assuming the stretched exponential functions, making it possible to evaluate the conformational exchange rate from all-*trans* zigzag form to the statistical *trans–gauche* form. In the case of VDF 50-u model at 450 K, the relaxation function could be fitted by the following function as shown by the thin solid line in Fig. 4

$$\mathit{Trans}\ \text{ratio} = a + b\cdot\exp\left[-\left(\frac{t}{\tau}\right)^{\alpha}\right]$$

$$= 0.404 + 0.552\cdot\exp\left[-\left(\frac{t}{15.32}\right)^{0.79}\right] \quad (3)$$

In the case of VDF 70-u model at 500 K, the relaxation function was obtained as given below

$$\mathit{Trans}\ \text{ratio} = 0.299 + 0.736\cdot\exp\left[-\left(\frac{t}{8.65}\right)^{0.79}\right] \quad (4)$$

The relaxation time of the VDF 50-u model is $\tau = 15.3$ ps at the phase transition temperature and is longer than 8.7 ps of the VDF 70-u model. This means that the VDF 70-u model can achieve faster to the equilibrium state than the VDF 50-u model. In other words, the cooperative structural change can occur more drastically in the VDF 70% copolymer case compared with the VDF 50% copolymer.

Fig. 5 shows the temperature dependence of the MD cell volumes calculated for VDF 50 and 70 mol% models. With a rise of temperature, the cell volumes increased gradually. At the phase transitional temperature, the cell volumes

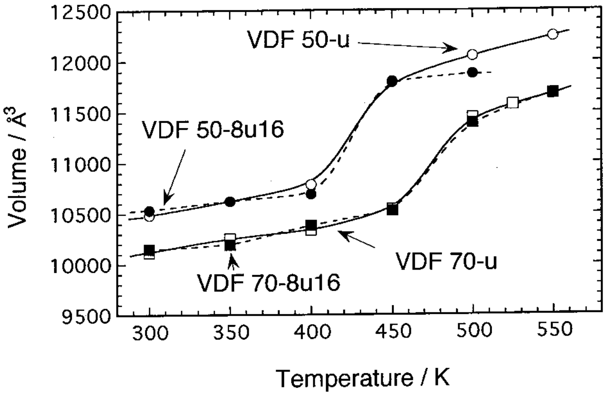


Fig. 5. Temperature dependence of the cell volumes calculated for VDF 50 and 70%-TrFE copolymers (Type I models).

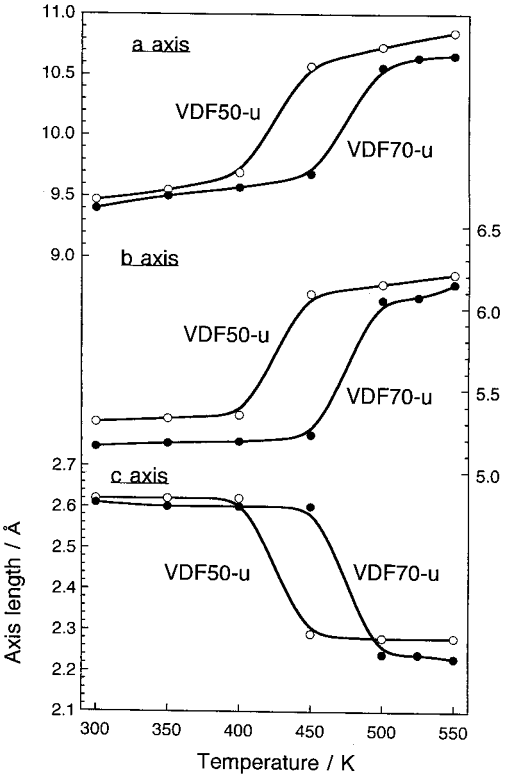


Fig. 6. Temperature dependence of the axis length calculated for VDF 50 and 70%-TrFE copolymers (u models).

increased remarkably. Fig. 6 shows the temperature dependence of the unit cell parameters of VDF 50-u and VDF 70-u models. In the low temperature range, the *a*- and *b*-axial lengths increased gradually with temperature. At the phase transitional temperature these lengths increased drastically. On the other hand, the *c*-axis length decreased because of the generation of *gauche* conformations in the extended all-*trans* chains. For both the LT and HT phases the cell volume of the VDF 50% model is larger than that of the VDF 70% model because of Coulombic repulsion between fluorine atoms in the neighboring chains.

The *a*/*b* ratio in the HT phase is calculated for these two copolymers as follows

VDF 50-u model

$a = 10.57$ Å, $b = 6.09$ Å, $c = 4.58$ Å and $a/b = 1.735$

VDF 70-u model

$a = 10.56$ Å, $b = 6.05$ Å, $c = 4.48$ Å and $a/b = 1.745$

where the *c*-axial length is doubled for the comparison with the experimental data. The experimentally-measured cell parameters of the HT phase are almost common to the copolymer samples with different VDF content [20]: $a = 9.75$ Å, $b = 5.63$ Å, $c = 4.60$ Å and $a/b = 1.73$. The calculated values are in fairly good agreement with these observed values. The a/b ratio $= 1.73$ ($= \sqrt{3}$) indicates the hexagonal packing of the chains in the HT phase as clarified by the X-ray studies.

3.2. Molecular motions of chains

3.2.1. Librational motion

In the present MD calculations, the molecular conformation in the HT phase was found to be a statistical combination of TG^+, TG^-, T_3G^+ and T_3G^- sequences. In the LT phase the molecular chain was in the all-*trans*-zigzag state and experienced the librational motions around the chain axis. In the HT phase the molecular chains rotated around the chain axis and sometimes changed the direction of the dipole moment of the molecular chain. These results reproduce quite well the experimental data. Fig. 7 shows the amplitude of the librational motion of an arbitrarily chosen molecular chain in VDF 50-u model at 300 and 500 K. In

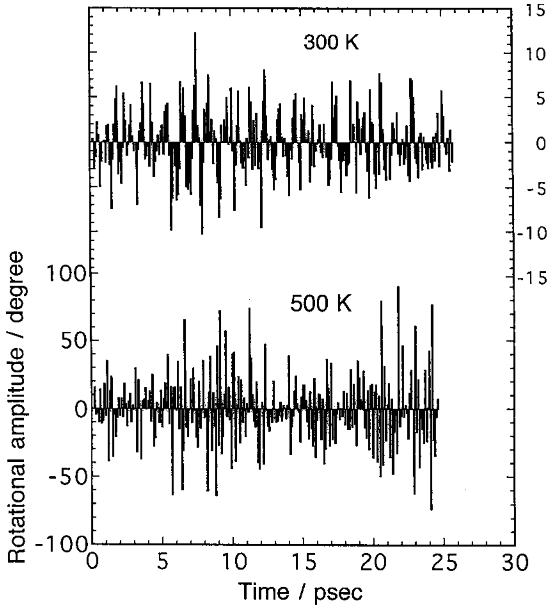


Fig. 7. Rotational amplitude of a molecular chain selected arbitrarily at 300 and 500 K for VDF 50-u model.

Table 2
Averaged amplitude and period of chains rotating around the chain axis in the LT phase

Model temperature (K)	VDF50-u		VDF70-u (1)	
	Rotation angle (°)	Period (ps)	Rotation angle (°)	Period (ps)
300	6.6	0.44	5.7	0.40
350	6.7	0.43	6.1	0.40
400	6.6	0.44	6.7	0.41
450	–	–	7.2	0.40

the LT phase the molecular chains oscillate around their chain axes with the averaged rotational amplitude of ±6.6°. The amplitude of the librational motion changes sinusoidally with time. The molecular chain rotates with undulation, sometimes largely and sometimes small. For example, at 300 K, the amplitude was 12° at 7 ps and 5° at 15 ps and 7° at 20 ps. In the HT phase, the molecular chains rotate more vigorously. The rotational amplitude becomes larger than that in the LT phase, because of coupling with the drastic conformation change of the chains of T $\rightleftarrows$ G. For example, at 500 K, the amplitude was 20° at 4 ps, 75° at 10 ps and 20° at 16 ps and 80° at 22 ps. The rotational amplitude at 500 K is about five times larger than that at 300 K. The mean amplitude of the rotational angle and the corresponding period is shown in Table 2 for each model in the LT phase (300–450 K). These rotational motions correspond to the librational motion. The period is 0.43 ps for VDF 50-u model and 0.41 ps for VDF 70-u model, corresponding to the librational frequencies of 76 and 83 cm^{-1}, respectively. The librational frequency observed experimentally by the far-infrared spectroscopy is 70 cm^{-1} for VDF 82 mol% copolymer and 60 cm^{-1} for VDF 72 mol% copolymer at room temperature [21]. Although the calculated values cannot be compared directly with these experimental values because of the difference in VDF content, this simulation can reproduce reasonably the tendency that the frequency is lower for the VDF–TrFE copolymer with lower VDF content. As the TrFE content is higher, Coulombic interaction is larger between the neighboring chains and the volume becomes larger. Then, larger free space is produced, making the rotational motion easier. That is to say, the librational frequency should be increased by increasing Coulombic interaction. But we have to consider also the effect of mass of the whole chain, which increases largely for the copolymer of higher TrFE content and so the chains rotate more slowly. Because of the balance between these two effects, larger free volume and heavier molecular chain, the librational frequency is considered to be lower for the copolymer of lower VDF content.

Table 3 lists the mean square displacements of carbon atoms calculated at the various temperatures. The atomic displacement was calculated as the difference between the atom position at every moment and the averaged position of the corresponding atom in the equilibrium state. In the LT phase the mean square displacement is smaller in the direction of the *a* and *b* axes than that of the *c* axis. The movement of the chains in the directions of the *a* and *b* axes is limited because of the electrostatic repulsion between the neighboring chains. All the molecular chains are allowed to move randomly only along the *c* axis direction. Therefore the translation along the *c* axis is extremely larger than that along the *a* and *b* axes. On the other hand, in the HT phase, the mean square displacement is larger in all the directions of the *a*, *b* and *c* axes, because the molecular motion is coupled with the rotational motion of the chain around the chain axis. In the LT phase, the mean square displacement of the carbon atoms in the direction of the a and the *b* axes is in the following order: $CH_2 \geq CF_2 \geq CFH$ for VDF 50-u, and $CF_2 > CH_2 \geq CFH$ for VDF 70-u. Strictly speaking, the all-*trans* chain takes the deflected conformation due to the interaction between two fluorine atoms in the adjacent CF_2 units. As shown in Fig. 8, the fluorine atoms 1 and 2 of VDF monomer unit can move relatively flexibly to avoid the overlapping with the fluorine atoms 3 and 4, respectively.

Table 3
Mean square displacement of carbon atoms of chains

Model direction (axis) (temperature/K)	VDF50-u			VDF70-u(1)		
	a (Å^2)	*b* (Å^2)	*c* (Å^2)	*a* (Å^2)	*b* (Å^2)	*c* (Å^2)
CH_2						
300	0.132	0.049	2.56	0.114	0.033	0.34
350	0.143	0.070	1.02	0.117	0.039	2.10
400	0.149	0.080	2.56	0.125	0.064	1.42
450	0.505	0.400	4.85	0.190	0.062	3.07
500	0.656	0.409	4.91	0.545	0.395	3.77
550				0.461	0.447	3.60
CF_2						
300	0.130	0.048	2.56	0.122	0.032	0.34
350	0.139	0.068	1.03	0.117	0.039	2.10
400	0.148	0.078	2.56	0.130	0.061	1.42
450	0.451	0.331	4.83	0.188	0.061	3.06
500	0.604	0.344	4.84	0.493	0.348	3.79
550				0.422	0.390	3.65
CFH						
300	0.120	0.047	2.55	0.109	0.031	0.34
350	0.123	0.068	1.03	0.096	0.038	2.10
400	0.139	0.078	2.56	0.157	0.062	1.43
450	0.434	0.318	4.84	0.157	0.057	3.06
500	0.566	0.313	4.88	0.440	0.363	3.82
550				0.430	0.333	3.58

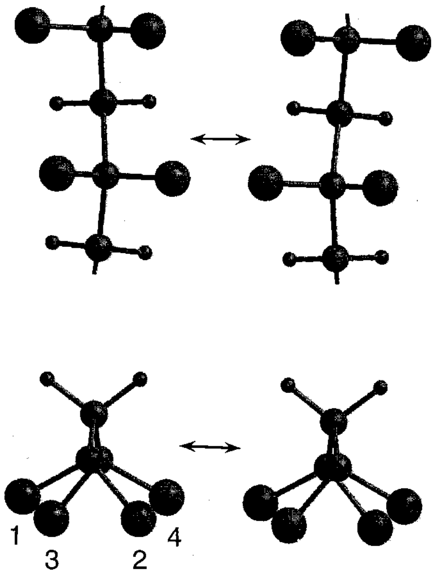


Fig. 8. An illustration of a deflection motion of a zigzag chain.

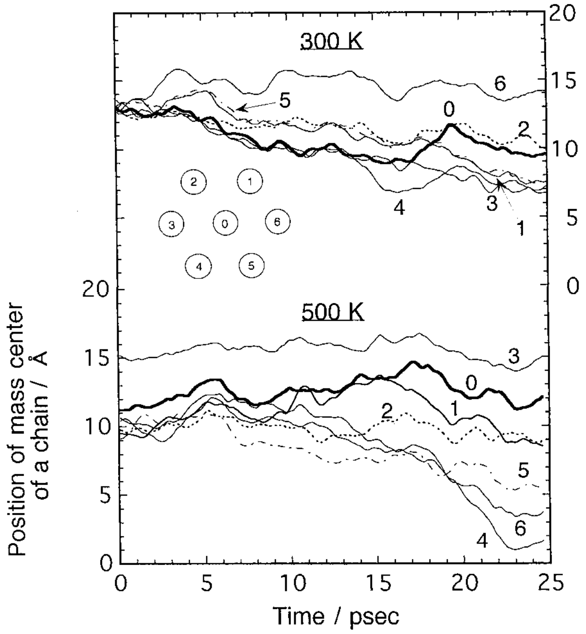


Fig. 9. Time dependence of the *c*-axis positions of the center of mass of the seven neighboring molecular chains of VDF 50-u model.

On the other hand, two hydrogen atoms in the adjacent CH_2 units can stay at the same position. Therefore, in the case of the VDF 70-u model, the mean square displacement of the carbon atom of CF_2 unit is larger than that of CH_2. As TrFE content becomes higher, the number of F atoms increases also in the CH_2 side, inducing higher disorder from the all-*trans* conformation. That is to say, as VDF content decreases, it is difficult to distinguish the CF_2 side from the CH_2 side in a chain. The mean square displacement of the carbon atoms of CH_2, CF_2, and CHF units is more similar to each other, as seen for the case of VDF 50-u model.

3.2.2. Translational motion

The translational motion of the whole chain along the chain axis was investigated by calculating the shifts of the center of gravity for a molecular chain chosen arbitrarily and the six molecular chains surrounding it. Fig. 9 shows the results for the VDF 50-u model at 300 and 500 K. In the LT phase there is no translational motion larger than 2.5 Å in the *c* axis direction. This limitation comes from the energy barrier caused by the regularly repeating structure with the period of 2.5 Å. On the other hand, in the HT phase, the chains shift in a wide range. In this phase the repeating period is lost by the invasion of *gauche* conformation. Every chain can make a large translational motion along the *c* axis direction.

3.2.3. Torsional motion

In Fig. 10 is shown the time dependence of the dihedral angles of arbitrarily chosen three bonds of a chain of the VDF 50-u model at 500 K. There are some particular patterns in the conformation change. For example, one bond keeps T(G) state all the time, one bond changes from T(G) to G^+ or G^-(T) state, and one bond changes from G^+ to T and again to G^+ state. The conformation change like $G^+ \rightarrow T \rightarrow G^-$ occurred a few times in the type I models. The MD calculation using the large chains (type II model) was performed in order to make the effect of the molecular sequence on the conformation change clear. The phase transition temperature of this model was about 400 K. In the equilibrium state at 425 K after the phase transition, the conformation change of $G^+ \rightarrow T \rightarrow G^-$ was observed in the molecular sequences of CF_2–CH_2–CF_2–CHF and CH_2–CF_2–CH_2–CF_2. This large conformation change was not observed for the sequences C–CFH–CF_2–C because of the higher rotational energy barrier around the bond. Table 4 lists the ratio of T, G^+, and G^- conformations calculated for the VDF 50-u and VDF 50-u20mer (type II) models in the HT phase. The sequences CH_2–CF_2–CH_2–CF_2 and CFH–CF_2–CH_2–CF_2 take the T, G^+, G^- states at almost the same ratio. On the other hand, the sequences of CH_2–CF_2–CFH–CF_2 and CF_2–CFH–CF_2–CFH take the T state at higher ratio than the G^+ or G^- state. This is independent of the chain length.

At this stage we can describe the concrete motion of the molecular chains experiencing in the phase transition as below.

Table 4
Ratio of T, G + , and G − of chains in the HT phase

Model conformation	VDF 50-u			VDF 50-u20mer		
	T	G +	G −	T	G +	G −
CH_2–CF_2–CH_2–CF_2	0.36	0.33	0.31	0.25	0.32	0.43
CH_2–CF_2–CFH–CF_2	0.58	0.23	0.19	0.49	0.14	0.37
CFH–CF2–CH_2–CF_2	0.43	0.25	0.31	0.29	0.21	0.50
CF_2–CFH–CF_2–CFH	0.68	0.15	0.17	0.64	0.14	0.23

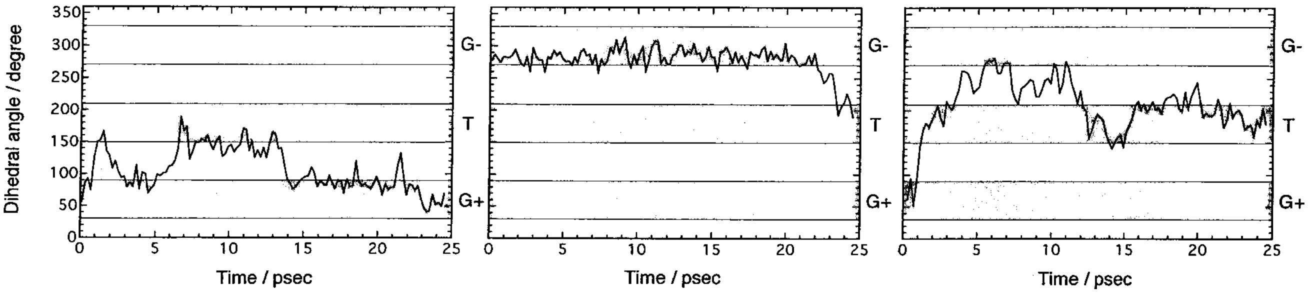


Fig. 10. Time dependence of the dihedral angles calculated for arbitrarily selected three bonds of a chain at 500 K of VDF 50%-TrFE copolymer (u model).

In the LT phase the molecular chains move up- and downward within the limit of 2.5 Å and, at the same time, rotate around their chain axes with an averaged amplitude of 14° as if they are trapped in the cylindrical space (Fig. 11). As the temperature rises, the movement of the atoms becomes violent and the space of movement is extended cooperatively. At a certain temperature, the space around the molecular chain becomes enough large to cause the conformational change from T to G. This conformational change occurs at first in the sequence of $-\mathrm{C{-}CH_2{-}CF_2{-}C}-$ because of the strong repulsive interaction between the neighboring chains. In the HT phase the molecular chains rotate violently around their chain axes, which couple with the conformational change. As a result, the dipole moment of the whole system disappears to zero.

By carrying out the NMR measurement, Ishii et al. proposed the following motions [22–24]. In the low temperature region of 30–80°C, the mobile fraction of the chain is about 20% at most. In the region of 80–114°C below the phase transition temperature, the mobile fraction increases higher because of an oscillation motion of VDF groups of *trans*-zigzag chains with an amplitude of 10°. As the temperature approaches the transition point, the mobile fraction increases up to 100%, indicating an active chain motion in the crystalline region through the T–G conformational exchange. Hirschinger et al. [25,26] proposed a three-body crankshaft motion such as $\mathrm{TGTG^{-}T \rightleftarrows TG^{-}TGT}$ for the molecular motion in the HT phase. Legrand et al. [27–29] analyzed the experimental data of elastic and quasi-elastic incoherent neutron scatterings for VDF 70% copolymer. The hydrogen atoms experience a diffusion motion within a cylinder of finite size. In the LT phase, the radius and height of the cylinder are 1.5 and 2.5 Å, respectively, and about 60% of the protons are spatially frozen in the sample. In the HT phase, the radius and height of this cylinder increase to 2.0 and 3.3 Å, respectively, and the mobile protons are about 87%. The molecular chains rotate around the chain axis combined with a transitional motion along the chain axis.

Our description of the molecular motion is quite consistent with all these experimental results. In other words we may succeed to simulate the essential feature of the structural change and molecular motion in the ferroelectric phase transition of VDF–TrFE copolymers through the MD calculations.

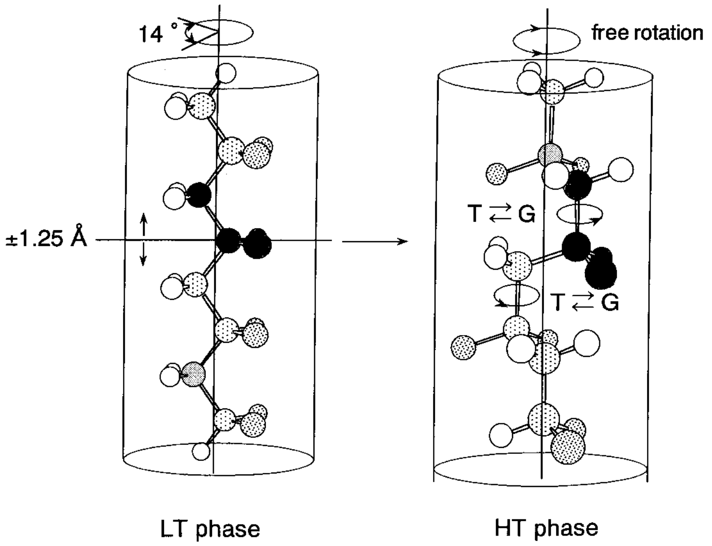


Fig. 11. An illustration of molecular chain motion coupled with the torsional motion in the ferroelectric phase transition of VDF–TrFE copolymer, which was deduced by the MD calculations.

4. Conclusions

In the present study the MD simulations were performed for the VDF–TrFE copolymer models of VDF 50 and 70 mol% content. The *trans*-to-*gauche* conformational change was observed to occur drastically and cooperatively at high temperature. It was found that the phase transition contains two important features: the *trans*-to-*gauche* conformational change and the rotational motion of the chains. The detailed analysis of the calculated results revealed that the conformational change occurs more easily in the regular VDF sequential parts than in the TrFE parts. It was also found that the hexagonal packing mode and the statistical combination of the TG^+, TG^-, T_3G^+, and T_3G^- conformational sequences of the molecular chains can be realized in the HT phase. All the structural changes observed in this MD calculation are reasonable compared with the experimental data reported by many researchers. We believe that we can clarify the common and essentially important characteristic features in the phase transitional phenomena of VDF–TrFE copolymers.

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