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Computer simulation of structure and ferroelectric phase transition of vinylidene fluoride copolymers. 5. Influence of orientational disorder of dipole moments and domain walls on phase transitional behavior

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Abstract

Molecular dynamics (MD) simulations have been performed in order to clarify the mechanism of ferroelectric phase transition in vinylidene fluoride–trifluoroethylene (VDF–TrFE) copolymers. Influence of orientational disorder of CF_2 dipoles and domain walls on the ferroelectric phase transition behavior has been investigated for VDF 50 mol.% copolymer system. Two types of MD unit cells were constructed by packing the 36 and 16 infinitely long chains, each of which consisted of random sequences of five VDF and five TrFE monomer units under the 3D periodic boundary conditions. For the models with all the CF_2 dipoles arrayed in parallel, the *trans*-to-*gauche* conformational change occurred at 450–500 K. Introduction of orientational disorder of one or two chains to the model, in which the dipoles are oriented into the opposite direction along the *b* axis, caused the reorientation of these dipoles to the original parallel direction at low temperature and the *trans*-to-*gauche* conformational change at 450 K. However, by making the dipole packing more irregular, the *trans*-to-*gauche* conformational change was found to occur quite easily even below the room temperature. An existence of the domain boundary, which was made in-between the domains consisting of the parallel packing of dipoles, was also found to cause similar structural changes. In this way, the irregular dipole array and/or the domain boundary were found to induce the *trans–gauche* structural transformation more easily at lower temperature, different from the models of regular dipole arrangements.

Keywords: Vinylidene fluoride copolymer; Ferroelectric phase transition; Disorder of dipole moment

1. Introduction

Poly(vinylidene fluoride) (PVDF) and the copolymers of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) or tetrafluoroethylene (TFE) are characteristic of their ferroelectricity and the related phase transitions. This phase transition is unique in such a point that the molecular chain conformation changes from all-*trans* zigzag form to disordered *gauche* form above the phase transitional temperatures [1–9], the so-called Curie temperature. Besides, the molecular chains rotate around the chain axis in the high-temperature paraelectric phase (HT phase). These structural changes induce the change of spontaneous polarization of the crystalline region and as a result, the electric properties such as piezo- and pyroelectricity disappear drastically above the Curie transition point.

It is important to clarify the microscopic mechanism of this characteristic structural transition. Computer simulation, especially molecular dynamics (MD) simulation is useful for structural investigation of the phase transition viewed from the molecular level under various conditions. In the previous papers [10–12], we determined the force field parameters adjustable for the simulation of the phase transition of VDF 50 and 70 mol.%-TrFE copolymers. Based on the obtained potential force fields, we carried out the MD simulation for the copolymers and confirmed that the phase transition can be described by the complicated combination of two such elements as the *trans*-to-*gauche* conformational change and the rotational motion of the chains. That is to say, the rotational motion was found to be strongly coupled with the *trans–gauche* conformation change. The *trans–gauche* conformational change occurred more easily in the regular VDF sequential parts than in the TrFE parts. In this way, we could reproduce the most important features of the phase transitional phenomena of VDF–TrFE copolymers by carrying out the MD simulation.

The next important problem was to clarify the factors governing phase transition. As already reported [13], VDF

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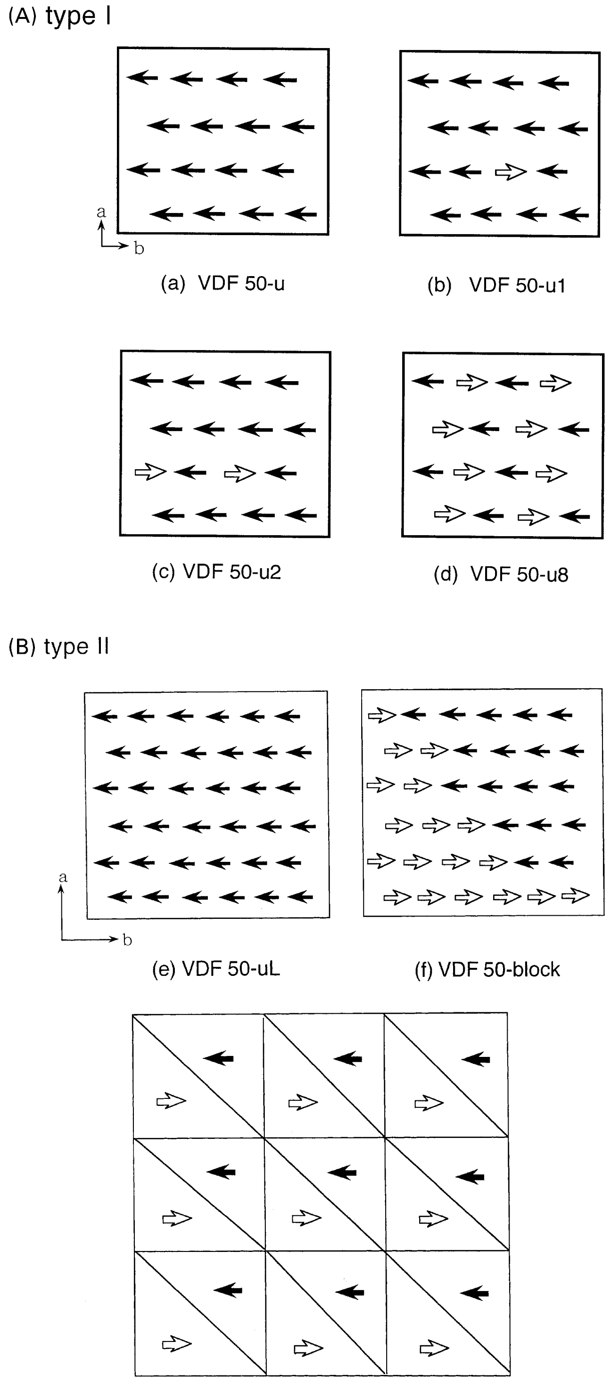

(A) type I

(a) VDF 50-u

(b) VDF 50-u1

(c) VDF 50-u2

(d) VDF 50-u8

(B) type II

(e) VDF 50-uL

(f) VDF 50-block

(g) Domain structure

Fig. 1. VDF(50)–TrFE copolymer models used in the simulation. The arrows indicate the dipole moments of the chains. Type I is the model consisting of 16 chains; (a) VDF 50-u, (b) VDF 50-u1, (c) VDF 50-u2, and (d) VDF 50-u8. Type II is the model consisting of 36 chains; (e) VDF 50-uL, (f) VDF 50-block, and (g) an illustrated image of the domain structure under the three-dimensional periodic boundary condition.

content of VDF–TrFE copolymers influences the phase transitional temperature. In a previous paper [14] we simulated the influence of the VDF content on the phase transition behavior and clarified the role of intra- and intermolecular interactions and the head-to-head and tail-to-tail (HHTT) abnormal linkage.

The crystallite size and/or the size of domains in the crystallite were pointed out as other important factors. Tashiro et al. [15] measured the DSC curves for various samples of VDF 65 and 73% copolymers annealed isothermally at different temperatures. The melting temperature (T_m) and the phase transitional temperature (T_C) changed largely depending on the annealing temperature: they increased as the crystallite size became larger. Ohigashi et al. [16] measured the DSC curves for the poled VDF 75% copolymer samples. The T_C shifted to a higher temperature side and the endothermic peak became sharper. Theoretically, Odajima et al. [17] derived an equation describing an effect of the crystallite size on the phase transitional temperature. The complicated motion of the chains was, however not taken into consideration. These studies suggested the significant role of the size and boundary of domains consisting of the dipole moments in the phase transitional behavior of the copolymers. In this paper we investigate the influence of the orientational disorder of the dipole moments and the domain wall on the phase transitional behavior on the basis of the MD simulation technique.

2. Simulation method

2.1. Force field

The force field parameters reported in a previous paper [11] 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 nonbonded interatomic interaction energies, i.e. the Coulombic interaction energy and van der Waals $1/R^6$ interaction energy were calculated by the ABCA Ewald procedure [18]. Repulsive van der Waals interaction energy was calculated within 7.6 Å. The total potential energy was calculated by summing up the energies of bond stretching, angle bending, torsional potential, and their cross terms [11].

2.2. Construction of models

In the present paper the VDF content was assumed to be 50 mol.% as a typical case. Two types of the MD cells were constructed. The type I models were constructed by packing the 16 chains, each of which consisted of random sequences of five VDF and five TrFE monomer units. The type II cell was constructed by packing the 36 chains, where each chain consisted of random sequences of five VDF and five TrFE monomers. According to the NMR analysis [19], VDF–TrFE copolymers are random as for the monomeric sequences of VDF and TrFE units in the molecular chains. Therefore, the monomer sequence of the molecular chain models was determined by a random number. The tacticity

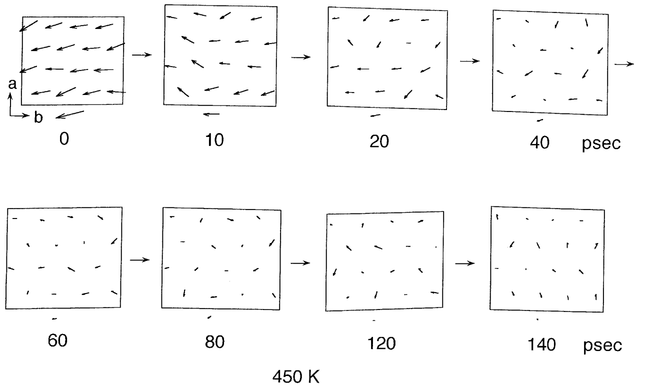


Fig. 2. Time dependence of the motion of dipole moments of the VDF 50%–TrFE copolymer chains viewed along the chain axis (u model). An arrow shown at the bottom of each figure indicates the total polarization viewed along the chain axis.

of TrFE monomers was assumed to be atactic. The monomer sequence in a chain was set independent of the other molecular chains. Three-dimensional periodic boundary condition was used for the MD unit cell. That is, the movement of every atom included in a unit cell was assumed to be the same in all the neighboring unit cells and to be able to pass through the walls of the cells. The first monomeric unit of a finite chain in a unit cell and the last monomeric unit of the corresponding chains in the adjacent unit cells along the *c* axis were connected by covalent bonds. Therefore, the models contained infinitely long chains along the *c* axis direction under the periodic boundary condition. In the normal models of the type I (VDF 50-u) and II (VDF 50-uL), all the CF_2 dipoles were arrayed in parallel along the *b*-axis. In these models the chains directed upward along the *c* axis, where the upward direction was defined in such a way that the direction vector of CH_2CF_2 monomeric units was pointed into the positive direction of the chain axis. In the disordered model of the type I structure, an orientational disorder of one, two, or eight chains was introduced to the model VDF 50-u so that these selected chain dipoles were directed in the opposite direction along the *b* axis. These models were named VDF 50-u1, VDF 50-u2, or VDF 50-u8 models, respectively, as shown in Fig. 1(a)–(d). In the type II model, an MD cell was divided into two domains, each of which contained the 18 chains with the dipoles directed to the opposite directions along the *b* axis (see Fig. 1(f)). A whole image of the domain structure constructed in this study is illustrated in Fig. 1(g) under the three-dimensional periodic boundary condition. The bold arrows represent the polarization obtained by summing up the dipole moments of 18 chains in one domain. The potential energies of the crystal structures were minimized by the conjugate gradient algorithm until the root-mean-squared (rms) values of the strain energy of the atoms and the stress of the unit cell became lower than the critical values of 0.01 kcal/mol Å and 0.01 GPa, respectively.

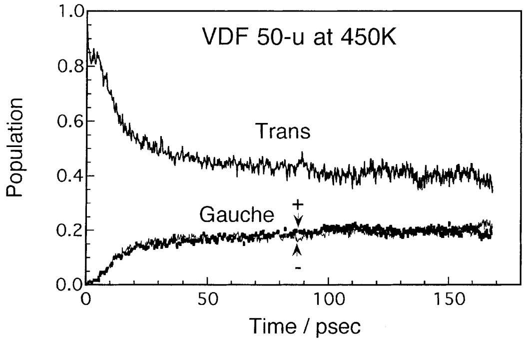


Fig. 3. Time dependence of the *trans* and *gauche* fractions in the molecular chains calculated for VDF 50-u model at 450 K.

2.3. Molecular dynamics calculation

MD simulations were performed on the basis of the Parrinello–Rahman method of constant pressure and temperature [20] with a Nose–Hoover thermostat [21,22] at various temperatures between 250 and 550 K. In the present MD calculation, the temperature-jump method was performed. Starting from the minimized structure, the temperature of the system was increased rapidly to a predetermined value and the NPT ensemble calculation was made for about 20 ps. The time was elongated or shortened by judging whether the averaged conformational state was equilibrated or not. This process was repeated at different temperatures. The calculation at the next higher temperature was performed starting from the equilibrated structure in the last calculation. The trajectory including the coordinates and velocities of all atoms was recorded at every 0.1 ps.

3. Results and discussion

3.1. Phase transitional behavior of the normal model

The details of the treatment of the calculated trajectories were already described in previous papers [11,12]. At first, the structural change in the normal model VDF 50-u is described here as a typical example. Starting from the initial model obtained by the minimization method, the conformation change from the *trans* to *gauche* forms could not be seen at such low temperatures as 300–400 K. The molecular chains took the deflected *trans*-zigzag conformation and the CF_2 groups and/or the whole chains were found to librate with large amplitudes around the chain axes. Remarkable conformation changes were found at 450 K. The molecular chains changed their conformation from the extended *trans*-zigzag form to the twisted and kinked form containing both the *trans* and *gauche* bonds. Not only the change in the molecular conformation but also the rotational motion of the chains were detected. These changes resulted in the orientational change of CF_2 dipoles or the change of the electric dipoles. Fig. 2 shows the motion of the calculated dipole moments of all the chains of VDF 50-u model at

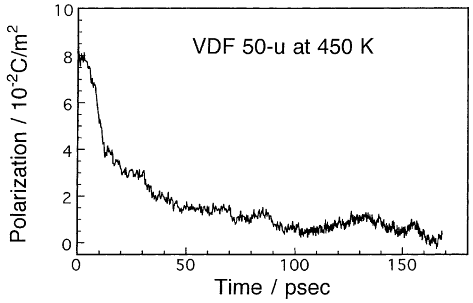


Fig. 4. Time dependence of the *b* axis component of the polarization calculated for VDF 50-u model at 450 K.

450 K. At the starting point of Fig. 2, the dipole moments of all the chains were almost equal in magnitude and oriented in parallel along the *b* axis. Until 20 ps the direction of each dipole moment was kept to the same direction, but the magnitude became gradually smaller because of the generation of the *gauche* bonds in the chain. After that, the dipole moments of the several molecular chains were observed to change the orientation direction largely and fluctuate around the chain axis. In the equilibrated stage of 100–170 ps, the dipole moments of very small values were found to rotate randomly. The population of *trans* and *gauche* bonds of the skeletal chains is plotted against time as shown in Fig. 3, where the *trans* and *gauche* angles were assumed to cover the torsional angles in the ranges of 150–210° (T), 30–90° (G^+), and 270–330° (G^-). The fraction of T was 1.0 at the starting point and it decreased steeply in a time region of about 10 ps. In parallel, the populations of G^+ and G^- increased in the same manner. At the equilibrated stage of ca. 130 ps, the distribution to the T, G^+, and G^- became almost constant; $T : G^+ : G^- = 40 : 20 : 20$. The time dependence of the b-axis component of the spontaneous polarization (P_s-b) is shown in Fig. 4 for the VDF 50-u model at 450 K. The dipole moment of each chain was calculated by the following equation.

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

where $Q_j(k)$ and $\vec{X}_j(k)$ are an electric charge and a Cartesian coordinate vector of each atom j belonging to the kth 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 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 value 8×10^{-2} C/m^2 at the initial state of MD calculation is in good agreement with this value.

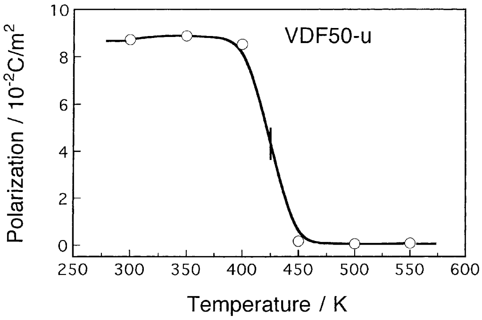


Fig. 5. Temperature dependence of the *b* axis component of the polarization calculated for VDF 50-u model.

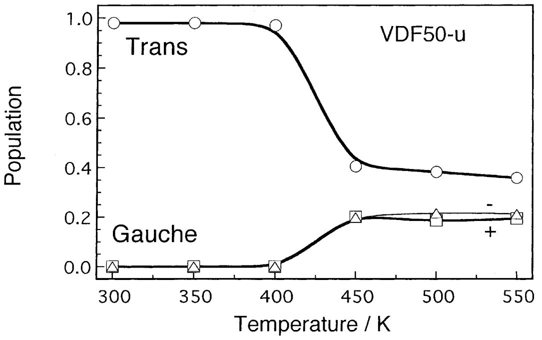


Fig. 6. Temperature dependence of the *trans* and *gauche* bond fractions calculated for VDF 50-u model.

The temperature dependence of P_s-b evaluated from an equilibrated state is shown in Fig. 5. In the low temperature region the P_s-b was almost constant and decreased drastically around 425 K. In Fig. 6 is shown the temperature dependence of the population of the *trans* and *gauche* bonds of the skeletal chains in the equilibrated state. The ratio of T was almost unity in the low temperature region and decreased drastically above the phase transitional temperature.

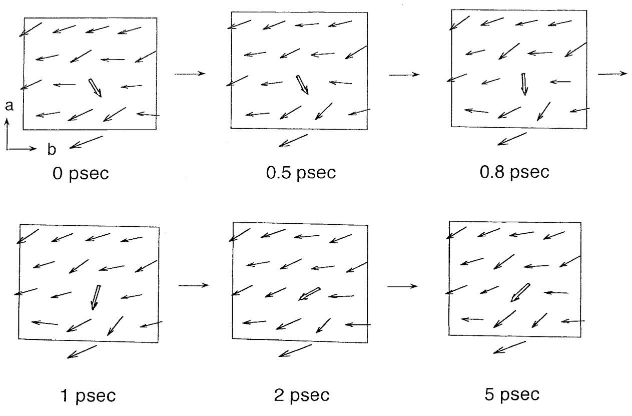
Before discussing the effect of various factors on the phase transitional behavior of this copolymer, we must notify here again the calculated values of the phase transition temperature. As already pointed out in the previous papers [11,12], the transition point evaluated by the MD calculation depends on the model used in the calculation. In the actual sample, many upward and downward chains with different VDF sequences are packed in a statistically random manner. In the MD calculation, we have to construct the crystal structure models of finite size. Ideally, we should build the models containing as many number of chains as possible in order to realize the perfect randomness of the molecular chain packing. In such a sense, the models consisted of 16 or 36 chains, which was adopted here within the limitation of the memory size and cpu time of the computer, may be too small to satisfy this requirement. But, we may say definitely that even if the present models were small in size, the essential features of the phase transition behavior could be obtained quite reasonably. Roughly speaking the phase transition temperature may be estimated within an error of ±50 K for various kinds of models constructed for a copolymer with a particular VDF content.

3.2. *Influence of the orientational disorder of dipole moments*

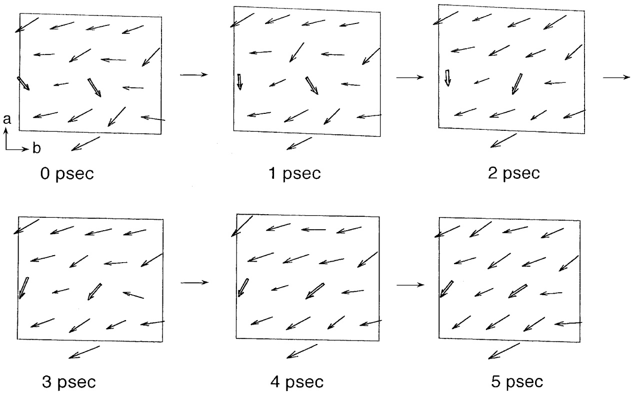
When MD calculation was performed for VDF 50-u1 model at 250 K, the chain dipole, which was initially oriented in the opposite direction along the *b* axis, rotated rigidly and as a result the chain dipole turned very quickly to the same direction with the others. In Fig. 7(a) is shown the motion of the calculated dipole moments of all the chains at 250 K, projected on the plane perpendicular to the chain axis. At the starting point, the dipole moments of all the chains were almost equal in magnitude and oriented in parallel along the *b* axis except one chain directing in the opposite direction. (Exactly speaking, the dipole vector of this unique chain was not parallel to the *b* axis but directed about 45° from the *b* axis after the performance of the energy minimization as a result to avoid the instability due to the electrostatic repulsion.) It took about 2 ps for this dipole to change the orientation in the direction of the other dipoles. After that, the chain librated around the chain axis. During the reorientation and libration, the chain kept the *trans* (T) form although some skew (S) bonds were generated also. In the six chains surrounding the disordered chain, some *gauche* (G) bonds were also generated momentarily.

In the case of VDF 50-u2 model, the two chains with the oppositely directed dipoles along the *b* axis started to rotate rigidly and the dipole directions changed toward those of major dipoles within about 5 ps at 300 K (see Fig. 7(b)). During the rotational motion, the two chains kept the T form. After that, the two chains continued to librate around their chain axes while still keeping the T form. In the cases of VDF 50-u1 and VDF 50-u2, the *trans*-to-*gauche* transitional temperature was about 425 K, the same as that of the VDF 50-u model and did not shift irrespective of the misorientation of the dipoles.

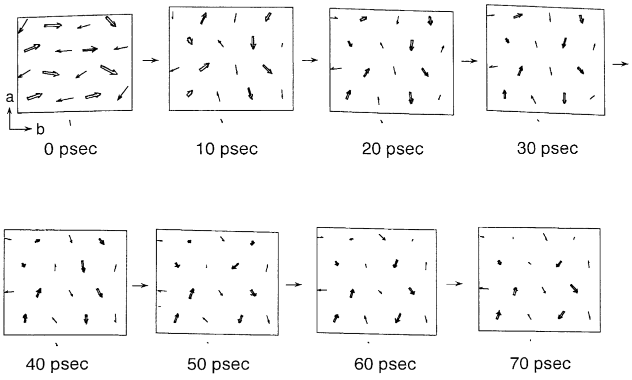
As an extreme case, the MD calculation was performed by using VDF 50-u8 model, where eight chains were packed with their dipoles directing oppositely along the *b* axis (Fig. 1(d)). In this case, the *trans*-to-*gauche* conformational change was found to occur quite easily even below the room temperature. Fig. 7(c) shows the time dependence of the motion of dipole moments at 250 K. In this case, some *gauche* bonds appeared in each chain and the chains rotated randomly. In the case of the normal model of VDF 50-u, the molecular chains kept the *trans* form at 300–400 K and changed to the *gauche* form at 450 K. The ratio of *trans* (T) and *gauche* $(G^+$ and $G^-)$ in the equilibrium state was $T : G^+ : G^- = 70 : 15 : 15$ at 250 K in VDF 50-u8 model, and 40:20:20 at 450 K in VDF 50-u model. Obviously, the structure of VDF 50-u8 at 250 K can be assumed as a transient state transforming to the conformationally-disordered HT phase.



(a) VDF 50-u1 at 250 K



(b) VDF 50-u2 at 300 K



(c) VDF 50-u8 at 250 K

Fig. 7. Time dependence of the motion of dipole moments of the VDF 50%–TrFE copolymer chains (16 chains model) viewed along the chain axis: (a) VDF 50-u1, (b) VDF 50-u2, and (c) VDF 50-u8. An arrow shown at the bottom of each figure indicates the total polarization viewed along the chain axis.

For both the cases of VDF 50-u1 and VDF 50-u2 models, the oppositely-directed *trans*-zigzag chains were found to turn back in a few ps to the main orientation direction of the surrounding other chains. Such a fast rotation of zigzag

Table 1
Energy and volume of the minimized models

Model	Energy (kcal/mol m.u.)[a]				Volume (Å^3/m.u.)
	Total	VdW	Coulomb	Valence	
(a) Type I					
VDF 50-u	−75.91	−0.47	−83.01	7.57	62.04
VDF 50-u1	−75.59	−0.38	−82.90	7.69	62.63
VDF 50-u2	−75.54	−0.31	−82.99	7.76	63.17
VDF 50-u8	−53.45	−0.21	−60.66	7.42	66.53
(b) Type II					
VDF 50-u	−75.63	−0.41	−82.84	7.62	62.75
VDF 50-block	−74.51	−0.09	−82.42	8.00	64.46

[a] m.u.: monomer unit.

chain is not detected in the dielectric relaxation measurement: the relaxation time due to the chain rotation is reported to be an order of ns in the high-temperature phase and ms at 250 K [2]. This implies that such a situation as models u1 and u2 is energetically unstable and cannot be realized in the actual crystal.

The case of VDF 50-u8 model is also unstable and changes immediately to the packing structure of conformationally-disordered chains. The reason can be seen in Table 1, where energy and volume are compared among various models after being minimized energetically. For the models of VDF 50-u, -u1 and -u2, as the orientational disorder of dipoles in the cell increases, the Coulombic interaction energy increases between the disordered chains and their neighboring chains. But this instability due to electrostatic interaction is relatively small. For VDF 50-u8 model, this instability is remarkably large, reflecting on the increase of cell volume. As reported in the previous paper [12], the large volume induces the *trans*-to-*gauche* conformational change at lower temperature. The similar situation could be seen also for VDF 50-u8 model.

3.3. Influence of the domain boundary

At first, MD calculation was performed for the normal model of type II, i.e. VDF 50-uL. In Fig. 8 is shown the energetically minimized structure of VDF 50uL and VDF 50-block models (refer to Fig. 1(e) and (f), respectively). In Fig. 9(a) and (b) are shown the time dependences of the motion of dipole moments of 36 chains at 300 and 500 K, respectively, which were obtained by the MD calculation for VDF 50-uL model. Although the skew form appeared sometimes, the molecular chains kept the *trans* form and librated around the chain axes at 300–450 K. The phase transition was detected at 500 K as seen in Fig. 9(b). In the case of the block model (VDF 50-block), in which the dipoles of 18 chains are packed in the opposite direction along the *b* axis in order to make the domain boundary as shown in Fig. 1(f), it was impossible to build the crystal structure consisting of the chains of all-*trans* zigzag conformation only. As shown in Fig. 8, after the energy minimization, the molecular chains located near the domain boundaries changed the direction of their dipole moments or generated the *gauche* bonds in their skeletal chains. These structural changes are considered to occur in order to remove the instability caused by the electrostatic interaction between the neighboring molecular chains. On the other hand, the molecular chains forming a long array along the *b* axis kept their CF_2 dipoles parallel to the *b* axis, even after the energy minimization. In Fig. 9(c) is shown the time dependence of the motion of dipole moments of the VDF 50-block model at 250 K. When the MD calculation was started, some *gauche* (+/−) bonds appeared rapidly even at such a low temperature as 250 K. But, the ratio of *trans* and *gauche* bonds in the equilibrium state was $T : G^+ : G^- = 70 : 15 : 15$. That is, the system didn't reach the HT phase consisting of the totally *gauche*-type chains. In Fig. 10 is shown the temperature dependence of population of *trans* and *gauche* forms of the type II models. In the case of the normal model VDF 50-uL, the ratio of *trans* bond was about 0.95 at 300 K. As the temperature of the system rose, the *trans* content decreased only slightly, but decreased drastically to ca. 0.4 at 500 K. In parallel, the total content of *gauche* bond increased to ca. 0.4 (G^+ 0.2 and G^- 0.2) at this temperature. In the case of the block model, the *trans* content decreased gradually with increasing temperature and the *gauche* bond increased in parallel. At 450 K, the

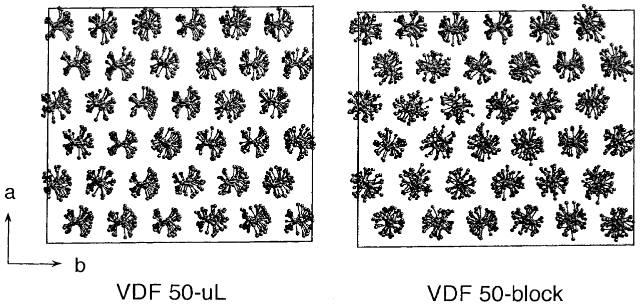
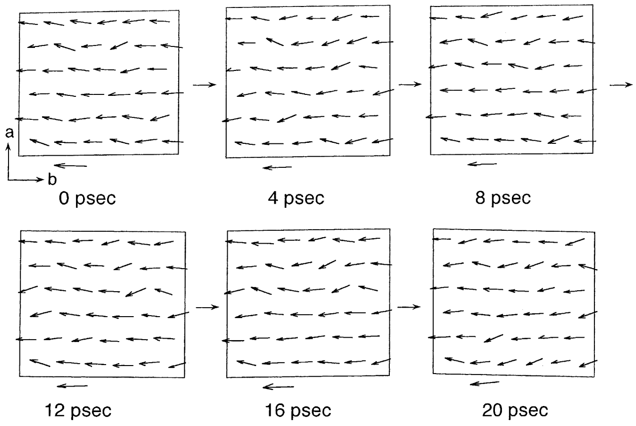
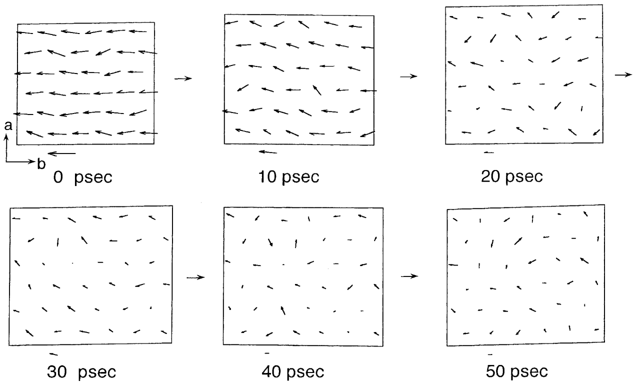


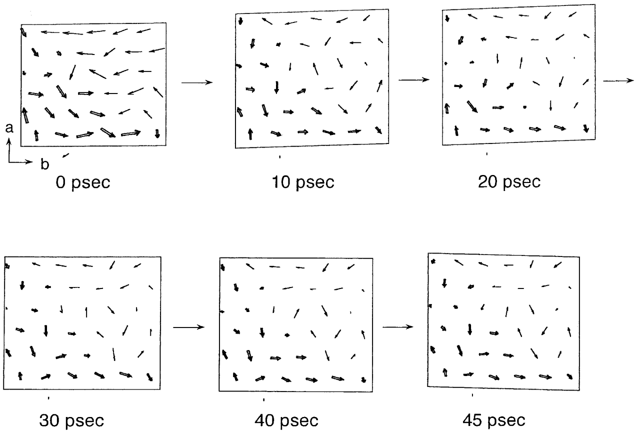
Fig. 8. Energetically-minimized crystal structures of VDF 50-uL and VDF 50-block viewed along the chain axis.



(a) VDF 50-uL at 300 K



(b) VDF 50-uL at 500 K



(c) VDF50-block at 250 K

Fig. 9. Time dependence of the motion of dipole moments of the VDF 50-uL and block models viewed along the chain axis: (a) VDF 50-ul at 300 K, (b) VDF 50-uL at 500 K, and (c) VDF 50-block at 250 K. An arrow shown at the bottom of each figure indicates the total polarization viewed along the chain axis.

ratio of *trans* and *gauche* bonds became $T : G^+ : G^- = 40 : 20 : 20$. In this way, the block model transferred to the HT phase continuously at lower temperature than the normal model. In Table 1 are shown the energy and volume of these two models. The VDF 50-block model is energetically more unstable because of higher energies of van der Waals and Coulombic interactions than the normal model (VDF 50-uL). These interactions expand the cell volume and the conformational change occurs more easily at low temperature.

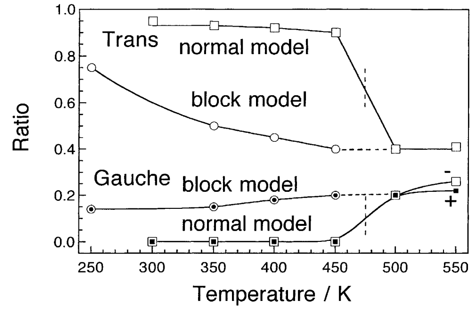


Fig. 10. Temperature dependence of *trans* and *gauche* conformation fractions calculated for VDF 50-uL and VDF 50-block models.

At this stage the VDF 50-block model reminds us the so-called cooled (CL) phase observed for VDF–TrFE copolymers with VDF molar content lower than 55%. This CL phase can be obtained by cooling the HT phase slowly to the room temperature [3,4]. Tashiro et al. proposed the superlattice structure for this CL phase, where the *trans*-zigzag chains (containing the conformationally-disordered parts) are packed together to form a

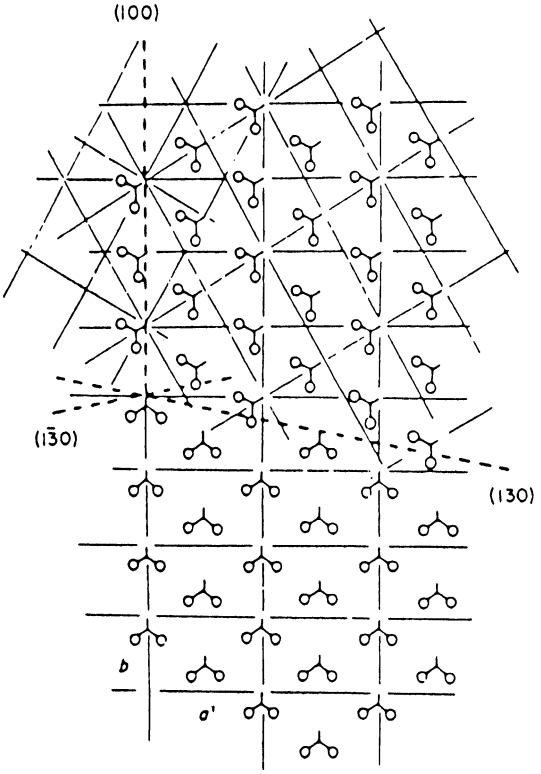


Fig. 11. Structural model of the cooled phase of VDF 55%–TrFE copolymer, showing the aggregation of domains with different orientations of *trans*-zigzag chain dipoles [4].

domain structure of finite size. As shown in Fig. 11, these domains are combined together at the boundary of (130) [and $(1\bar{3}0)$] plane. In the neighboring domains, the dipoles of chains are assumed to orient to the different directions at an angle of 60° from each other. This CL phase transfers to the HT phase continuously in a wide temperature region by heating. The existence of domains, the similar inner-structure of the domains, the angle of chain dipoles among the neighboring domains, and the continuous transition behavior from *trans* to *gauche* form, all these situations are found to be quite similar to the results obtained by the MD calculation made for the VDF 50-block model. So far, the reason why the CL phase transfers continuously to the HT Phase has not been understood clearly. But, by carrying out the MD simulation of VDF 50-block model, we may say that the essential feature of the CL phase could be clarified for the first time from the molecular level.

4. Conclusion

In the present paper, the MD calculation was made for the VDF 50 mol.% copolymer models with a different type of dipole orientational disorder. As the relative number of oppositely directing CF_2 dipoles was increased, the *trans*-to-*gauche* conformational change was found to occur at lower temperature. The dipole–dipole interaction destabilized the whole system and expanded the cell volume, resulting in the decrease of the transition temperature. A similar but more remarkable effect could be seen for the model with large wall in between the oppositely directed domains which were constructed by the parallel arrangements of the CF_2 dipoles. The *trans*-to-*gauche* conformational transition occurred at such a low temperature as 250 K and transformed to the high-temperature phase continuously in a wide temperature region. This behavior was found to be quite similar to that of the CL phase of VDF copolymers with low VDF content.

In this way, the disorder in the dipole orientation was found to have a serious effect on the phase transitional behavior of VDF–TrFE copolymers. This result suggests us a possibility of controlling the physical property of this copolymer system by controlling the molecular arrangement in the crystal lattice.

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