ELSEVIER

Polymer 43 (2002) 4783–4789

polymer

www.elsevier.com/locate/polymer

A theoretically reproduced phase diagram for vinylidene fluoride and trifluoroethylene copolymers

Susumu Ikeda*, Toshinao Yuki[1]

Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, Jonan 4-3-16, Yonezawa 992-8510, Japan

Received 22 February 2001; received in revised form 22 April 2002; accepted 9 May 2002

Abstract

The phase diagram of ferroelectric copolymers of vinylidene fluoride and trifluoroethylene is reproduced theoretically using a simple model for ferroelectric polymers. The copolymerization ratio dependencies of the intramolecular interaction and the intermolecular interaction are induced to reproduce the phase diagram. These interactions have the following effects on the ferroelectric phase transition of the copolymers. The intermolecular interaction between vinylidene fluoride segments is dominant in the ferroelectric phase transition. The intramolecular interaction, discriminating between different chain conformations, gives the phase transition a variety of characters, including first and second order phase transitions. The copolymerization ratio dependence of the intermolecular interaction is also numerically estimated by summing the interaction energy between all atoms. Comparing these two results, we discuss the size of a segment carrying an elementary process of the phase transition. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Ferroelectric polymer; Phase transition; VDF–TrFE copolymers

1. Introduction

Properties of polymers in a solid state depend equally on intermolecular interaction and intramolecular interaction, unlike in the liquid state and in solution where intramolecular interaction is dominant. In ferroelectric copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE), there is an interesting relationship between the copolymerization ratio and thermodynamic properties that is controlled by competition between these two interactions.

In order to understand the ferroelectric phase transition of polymers, we previously proposed a simple model whose transition is dictated by the ratio of intramolecular interaction to intermolecular interaction [1]. Using the same model and the same calculation scheme, we tried to depict a theoretical phase diagram for ferroelectric and paraelectric phases in VDF–TrFE copolymers. The phase diagram was derived experimentally by Koga and Ohigashi [2] who adopted temperature and copolymerization ratio as two independent parameters. Correlation between the phase transition and the copolymerization ratio of the copolymer shows the VDF ratio dependence of the intramolecular and intermolecular interactions.

The copolymerization ratio dependence of the intramolecular interaction can be conjectured with the aid of the theory of Farmer et al. [3] and the experiment of Tashiro et al. [4] but that of the intermolecular interaction has not been obtained, in particular it has not been obtained by experiment. Zhang and Taylor [5] derived the copolymerization ratio (VDF content) dependence of the intermolecular interaction from the copolymerization ratio dependence of phase transition temperature in VDF–TeFE (tetrafluoroethylene) copolymer. While a different model is used in the current study, the understanding that the copolymerization ratio dependence of the interaction can be derived from that of the phase transition temperature is along the same lines as their study.

In Zhang's work, chains of different conformation are assumed to differ in intermolecular interaction. In our study, however, the intermolecular interaction is assumed to be the energy difference between parallel and antiparallel pairs of planar zigzag chains. The polarization reversal phenomena in the ferroelectric phase of this copolymer have a very short time constant. It suggests the importance of the energy difference between parallel and antiparallel pairs of dipoles, even if the origin of the energy difference may not necessarily be an electrical interaction such as a

---

* Corresponding author. Tel.: +81-238-26-3065; fax: +81-238-26-3066. *E-mail address:* ikeda@yz.yamagata-u.ac.jp (S. Ikeda).

[1] Present address: Tohoku Pioneer Co., 4-3146-7 Hachimanpara, Yonezawa 992-1128, Japan.

PII: S0032-3861(02)00308-7

dipole–dipole interaction [6–8]. So it is reasonable to assume that the intermolecular energy difference between the parallel and antiparallel pairs plays an important role in the ferroelectric behavior of the system. This effect of intermolecular energy difference is generally accepted in the field of ceramic-type ferroelectrics and ferromagnetic materials.

Thus, we predict the copolymerization ratio dependence of the intermolecular interaction using the changes in the phase transition temperature and temperature hysteresis as related to the copolymerization ratio. We also derive the VDF fraction dependence of the intermolecular interaction in a mean field approximation that gives the key to simple interpretation. Finally, we calculate the intermolecular interaction by summing the Lennard-Jones potentials between all atoms in the copolymer. On the basis of the correspondence between the results and our model, the physical entity of the unit in our model is discussed.

2. Model and its properties

In the proposed model, each element constituting a system has a conformational degree of freedom and the ordered state of the system is constructed cooperatively by the interaction between elements [1,9]. The element can take two conformations: either a planar zigzag conformation (abbreviated as g for ground state) consisting of only a *trans* bonds, or a helix-like conformation (abbreviated as e for excited state) including both *gauche* and *trans* bonds [10, 11]. Therefore, the theory assumes that the g state contains a dipole moment, which has two directional degrees of freedom, g_1 and g_{-1}, whereas the e state does not contain the dipole moment but has multiplicity A, corresponding to the degree of degeneracy of the e state. The model has four configurations for a pair of elements: a parallel pair of g elements, an antiparallel pair consisting of g_1 and g_{-1} elements, a pair consisting of g and e elements, and a pair of e elements. In this system the interaction Hamiltonian is written as follows:

$$H = -V\sum_{i>j}\sigma_i\sigma_j + W\sum_i\left(1-\sigma_i^2\right). \tag{1}$$

Here, $\sigma(=1,0,-1)$ stands for a variable for a dipole moment. $\sigma = 0$ corresponds to the e state and $\sigma = 1$ and -1 correspond to the two directions of the dipole moment of the element in the g state. V stands for the amplitude of the intermolecular interaction between the elements and is assumed as the difference from the standard pair including the e state. The intermolecular interaction of the parallel pair is $-V$ and that of the antiparallel pair is V. W stands for an intramolecular interaction and since the standard is taken for the element in the g state, the element in the e state has the intramolecular interaction W.

The ferroelectric phase consists of only either g_{-1} or g_1, as can be seen directly from the model. The transition from the ferroelectric phase with a spontaneous polarization to a paraelectric phase without the spontaneous polarization includes two processes: an intramolecular mixing of *gauche* and *trans*, and an intermolecular mixing of g_1 and g_{-1}. For a depolarizing process including only the latter case, the phase transition is equivalent to that of the Ising model.

Due to the intramolecular mixing, this depolarizing process differs from the Ising model. In a previous study [1], we reported a new critical phenomenon which has a critical temperature at $T_c = 0.26T_{cI}$, where T_{cI} is the critical temperature of the Ising model. As the system approaches the new critical temperature, T_c, the phase transition varies from a first order phase transition to a diffuse transition through a second order phase transition with an increase in the ratio of intramolecular interaction to intermolecular interaction. This behavior represents the phase transitions that occur in a series of VDF–TrFE copolymers.

Also, a peculiar effect of polymers plays an important role in the phase transition of polymer crystals. According to Peterlin and Fischer [12], incoherent vibration of molecular chains smears out the potential energy well that catches atoms in polymer chains. The smearing out effect induces changes in the phase diagram and has a significant influence on the transition temperature.

3. Reproduction of transition behavior of VDF–TrFE copolymers

The ferroelectric–paraelectric phase transition of VDF–TrFE copolymers varies from a diffuse transition to a first order phase transition with increase in the VDF content in the copolymer. What is varied with the VDF content can be ascertained both theoretically and experimentally. Farmer et al. [3] predicted the following effect theoretically for a conformation of polyvinylidene fluoride (PVDF). PVDF takes a helix-like conformation (*trans*(t)–*gauche*(g)–t–g^*) when defects like head-to-head and tail-to-tail configurations are not included in the molecular chain. As defects increase, a planar zigzag conformation consisting of all *trans* bonds becomes more advantageous for the intramolecular interaction than the helix-like conformation consisting of *trans* and *gauche* bonds. In VDF–TrFE copolymers, however, Tashiro et al. [4] showed experimentally that the intramolecular interaction prefers the *gauche* bond to the *trans* bond in the high VDF content region and the *trans* bond to the *gauche* bond in the low VDF content region.

Both these results suggest that induction of TrFE monomers into PVDF alters the strength of the intramolecular interaction. This must affect the thermodynamic behavior of the copolymer. In a previous study we saw that the change in the thermodynamic order of the phase transition was induced by crossing the critical line in the

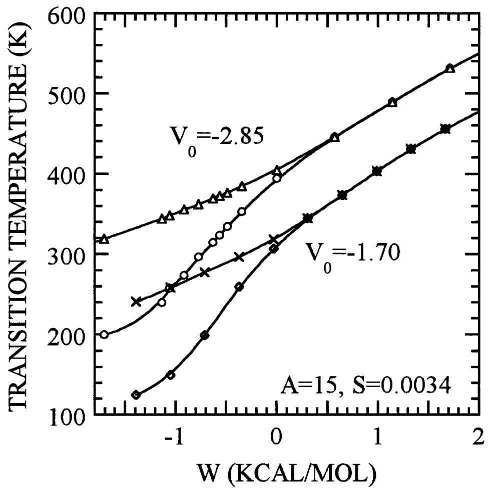

Fig. 1. Dependence of ferroelectric phase transition temperature on the intramolecular interaction. The intermolecular interactions V_0 (kcal/mol) were set at the two values specified in the figure. Both series separate into two branches near $W = 0.4$, above or below which the transition becomes diffuse or of the first order. The temperature difference of the two branches indicates the temperature hystereses, the phase transition during heating and cooling occur at the temperatures on the higher and lower branches, respectively.

transition map that is determined by the ratio W/V and multiplicity A [1].

The smearing out effect of the intermolecular interaction is formulated as

$$V = V_0 \exp(-SkT). \tag{2}$$

Here, S is described as

$$S = \frac{\pi^2}{5}\frac{N}{cd^2}, \tag{3}$$

where N is the number of chemical bonds along the c-axis, corresponding to the thickness of a lamella-type crystal, d is the distance between carbon atoms along the c-axis, and c is a force constant in the same direction.

From this point on, the value assumed for the multiplicity factor A is 15 and for the smearing out effect S is 0.0034. On the transition map [1], the critical line intersects the line $W/V = 0$ at $A = 10$, therefore, the transition in this case becomes diffuse in the region $W > 0$. In the results of the experiment conducted by Tashiro [4], the copolymer VDF65 has $W = 0$ and exhibits a clear first order phase transition. Therefore, the first order phase transition should occur even in the region $W > 0$, so we assume $A = 15$. The smearing out effect $S = 0.0034$ was selected by substituting 1000, 5×10^5 dyn/cm and 1.26 Å for N, c, and d in Eq. (3). $N = 1000$ means that crystals of VDF–TrFE copolymers have very large dimensions along the c-axis, far exceeding the 100 Å commonly seen in polyethylene crystals [14].

Thus, we derive the transition behavior of the VDF–TrFE copolymers by applying the Bethe approximation to the model. The procedure for calculation was described in detail in a previous paper [1].

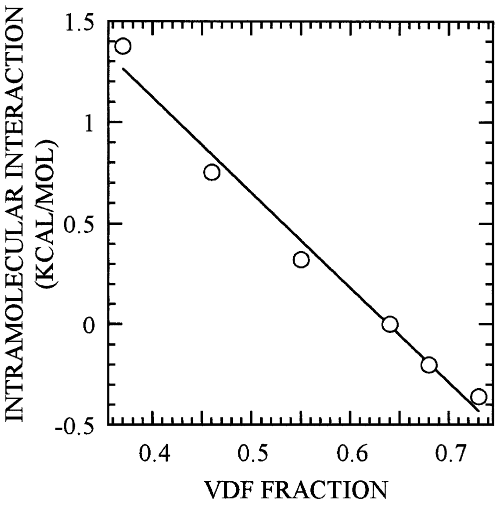

Fig. 2. Dependence of intramolecular interaction on the VDF fraction of VDF–TrFE copolymers.

Fig. 1 shows the phase transition temperatures that were estimated as a function of the intramolecular interaction. Intermolecular interaction is constant. The two lines correspond to the respective values of the intermolecular interaction. The intramolecular interaction was taken as the energy difference of the e state from the g state taken as the standard. Therefore, a positive intramolecular interaction means that the g state is more stable than the e state and a negative interaction implies the converse. In Fig. 1, the result shows that with an increase in the intramolecular interaction, the phase transition temperature shifts upwards and the temperature hysteresis decreases and disappears. Since the increase in the intramolecular interaction means lowering of the VDF fraction, the disappearance of the temperature hysteresis agrees with experimental findings but the upward shift in the phase transition temperature does not. In order to reproduce the phase diagram of the VDF–TrFE ferroelectric copolymers, both the intramolecular interaction and the intermolecular interaction must vary with the VDF fraction.

The copolymerization ratio dependence of the intramolecular interaction was assumed as shown in Fig. 2. Here, the value of the intramolecular interaction was assumed to vary the sign of the interaction near a VDF fraction of 65 mol%, as predicted by the experiment of Tashiro et al. [4] which showed that the intramolecular interaction is positive below 65 mol% VDF copolymer but negative above this value. The intramolecular interaction also has a rough linear dependence on the VDF fraction. This was designed to be consistent with the theoretical calculation of Farmer et al. [3], which resulted in the conclusion that the intramolecular interaction energy difference between the all *trans* conformation and the *tgtg** conformation is proportional to the content of head-to-head or tail-to-tail defect.

Once S is selected, the intermolecular interaction giving the critical temperature 338 K for the system with VDF 55 mol% is uniquely determined. The change in V_0 to

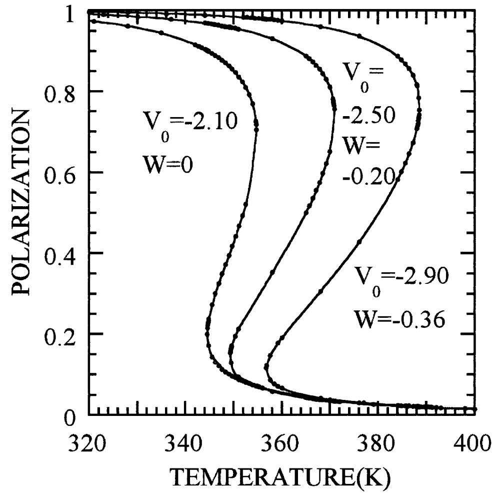

Fig. 3. Relationship between polarization and temperature of VDF–TrFE copolymers with high VDF content. These transition curves exhibit a first order phase transition with temperature hystereses. V_0 and W are specified in kcal/mol.

reproduce the temperature hysteresis and transition temperature is also determined. Thus we obtain the relation $P-T$ (P, spontaneous polarization) as shown in Figs. 3 and 4.

Fig. 5 shows the reproduced phase diagram. The solid lines were drawn by Koga and Ohigashi [2] using differential scanning calorimetry (DSC). The open circles in the figure show the phase transition temperatures obtained in this study. The experimental results show that the temperature hysteresis remains even in the region where the diffuse transition is occurring. This is sometimes observed in procedures such as DSC where the temperature of the system is changing with time and, therefore, it is thought that the temperature hysteresis does not have an intrinsic physical meaning here.

Fig. 6 shows the copolymerization ratio dependence of the intermolecular interaction V_0 that was used to reproduce the phase diagram.

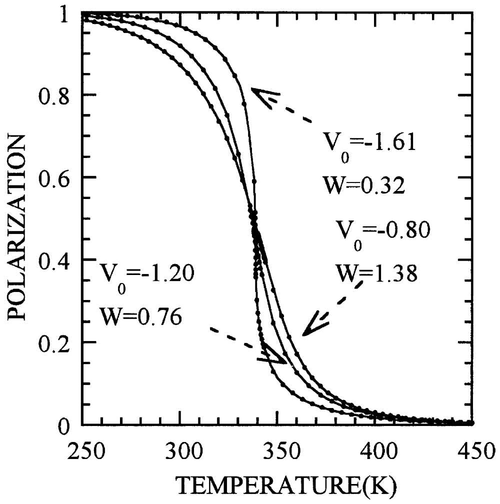

Fig. 4. Relationship between polarization and temperature of VDF–TrFE copolymers with low VDF content. These transition curves exhibit second order and diffuse transitions. V_0 and W are specified in kcal/mol.

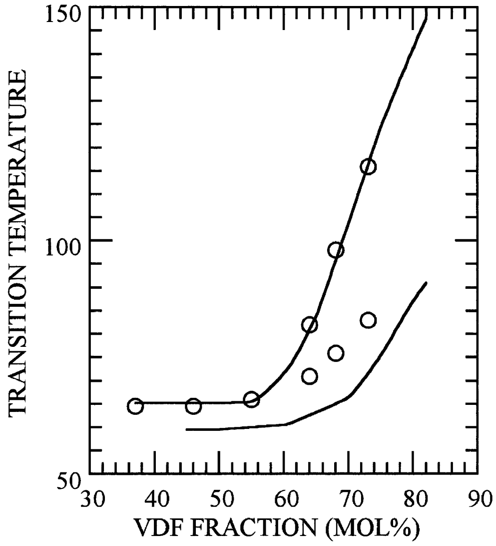

Fig. 5. Phase diagram of VDF–TrFE copolymers. Solid lines were depicted experimentally by Koga and Ohigashi. V_0 and W are specified in kcal/mol.

4. VDF fraction dependence of intermolecular interaction

In Section 3, we reached the conclusion that it is principally the VDF fraction dependence of the intermolecular interaction that controls the ferroelectric phase transition of copolymers of VDF and TrFE.

In this section, we consider the physical meaning of the VDF fraction dependence of the intermolecular interaction in two ways: first, in a mean field approximation to visualize the effect of each monomer and, second, in a molecular theoretical calculation to confirm the role of the intermolecular interaction.

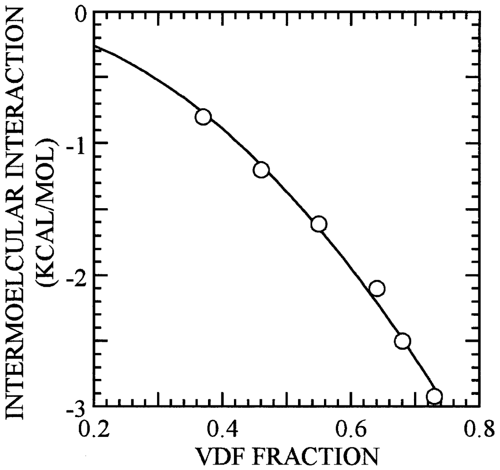

Fig. 6. Dependence of intermolecular interaction on the VDF fraction of VDF–TrFE copolymers. The solid line was drawn by substituting the values in Table 1 for Eq. (5).

Table 1
Constants of interaction strength of each pair represented in Eq. (4) (in kcal/mol). The values were determined to fit Eq. (5) to the data in Fig. 6

γ	β	α
−5.31	−0.04	−0.05

4.1. Mean field approximation

The intermolecular interaction $2V_0$ in our model was defined as the energy difference between the parallel and antiparallel pairs of the g elements in the model. Since the system under consideration is composed of VDF and TrFE monomers, an element in the model includes both monomers mixed in the ratios specified in the copolymer. Therefore, V_0 between the segments is given by averaging the interaction for a pair of VDF monomers, a pair of TrFE monomers and a pair comprising one VDF and one TrFE monomer. Interactions for these different pairs are denoted as γ for the VDF pair, β for the TrFE pair and α for the VDF and TrFE pair. The association probability between VDF monomers in a copolymer containing $100f$ mol% VDF was estimated as f^2 in the mean field approximation. From this we can estimate other association probabilities as $(1-f)^2$ for the pair of TrFE monomers, and $2f(1-f)$ for the VDF and TrFE pair. Then, the intermolecular interaction between copolymer segments including $100f$ mol% VDF is written as:

$$V_0 = f^2\gamma + (1-f)^2\beta + 2f(1-f)\alpha. \tag{4}$$

This equation is rewritten as:

$$V_0 = [(\gamma-\alpha)+(\beta-\alpha)]f^2 + 2(\alpha-\beta)f + \beta. \tag{5}$$

Unknown parameters in Eq. (4) are determined numerically to fit Eq. (5) to the VDF fraction dependence of V_0 in Fig. 6. Results are summarized in Table 1. The parameters are ranked $\gamma < \alpha < \beta$, and α and β are close to zero in comparison with γ. The principal intermolecular interaction controlling the ferroelectric properties is the energy difference between parallel and antiparallel pairs of VDF monomers.

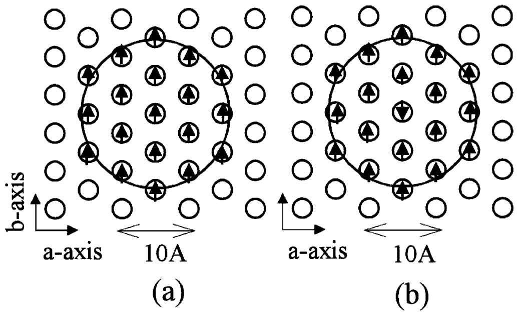

Fig. 7. Relationship between the center molecular chain and neighboring molecular chains. Arrows show the directions of the dipole moments of the molecular chains. Small circles correspond to the molecular section perpendicular to the molecular axis. The large circles have a radius of 10 Å and the Lennard-Jones interaction is calculated between the center segment and the atoms within the circle.

4.2. Molecular theoretical calculation of intermolecular interaction

4.2.1. Lennard-Jones interaction

The total intermolecular interaction of the system that includes various fractions of VDF was calculated as the sum of Lennard-Jones potential energy between all atoms within an assumed interaction length of 10 Å. The Lennard-Jones potential is:

$$u(r) = \varepsilon\left[\left(\frac{r_{\min}}{r}\right)^{12} - 2\left(\frac{r_{\min}}{r}\right)^{6}\right]. \tag{6}$$

Values of ε and $r_{\min}$ depend on the species of atom. The values for the potentials between atoms of the same species were as per Hasegawa et al. [15]. The values between atoms of different species were calculated by an empirical formula written as

$$r_{\min}(ab) = \frac{1}{2}[r_{\min}(aa) + r_{\min}(bb)], \tag{7}$$

and

$$\varepsilon(ab) = \sqrt{\varepsilon(aa)\varepsilon(bb)}. \tag{8}$$

For a polymer crystal consisting of M molecular chains, each of which is composed of $2N+1$ units, we have a total energy

$$U_{\text{total}} = \sum_{m=1}^{M-1}\sum_{m'>m}^{M}\sum_{i=-N}^{N}\sum_{j=-N}^{N} U(m_i, m'_j), \tag{9}$$

where $U(m_i, m'_j)$ is the sum of Lennard-Jones interaction energies described in Eq. (6) between all atoms in the ith unit in the mth molecule and those in the jth unit in the m'th molecule. The average interaction energy per unit is:

$$U_{\text{unit}} = \frac{1}{M(2N+1)}\sum_{m=1}^{M-1}\sum_{m'>m}^{M}\sum_{i=-N}^{N}\sum_{j=-N}^{N} U(m_i, m'_j). \tag{10}$$

Here, we consider the intermolecular interaction in the real copolymer system.

The crystal follows an orthorhombic system in all VDF fractions of the copolymer. In system we constructed, a molecule is composed of 100 carbon atoms and the random monomer sequence between VDF and TrFE is achieved through random numbers. The sequence of TrFE is atactic but excludes head-to-head or tail-to-tail defects. Each molecular chain includes the same VDF fraction but the sequences of monomers of VDF and TrFE differ.

In this system, the intermolecular interaction energy of the center chain was calculated for configurations both parallel and antiparallel to the surrounding molecules as shown in Fig. 7. The interaction between the monomers belonging to the same molecule was not considered because

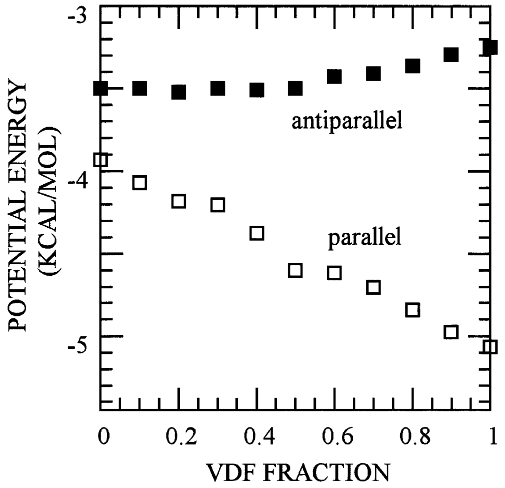

Fig. 8. Intermolecular potential energy calculated as a function of the VDF fraction.

this is categorized as an intramolecular interaction. The interaction between the units that are more than 10 Å distant from each other was neglected because of the short length character of the Lennard-Jones interaction. Thus, we can describe the intermolecular interaction per monomer unit working on the *m*th molecule as:

$$U(m) = \frac{1}{50}\sum_{i=1}^{50}\sum_{l_j(l\neq m,\, r_{m_i}-r_{l_j}<10\ \text{Å})} U(m_i, l_j). \qquad (11)$$

For the antiparallel configuration, the center chain was shifted by half of the lattice constant along the fiber axis after it was rotated by 180° because this configuration was energetically preferred.

The electrostatic interaction was not considered because it is well known that electrostatic interaction does not play an important role in the ferroelectricity of PVDF [13].

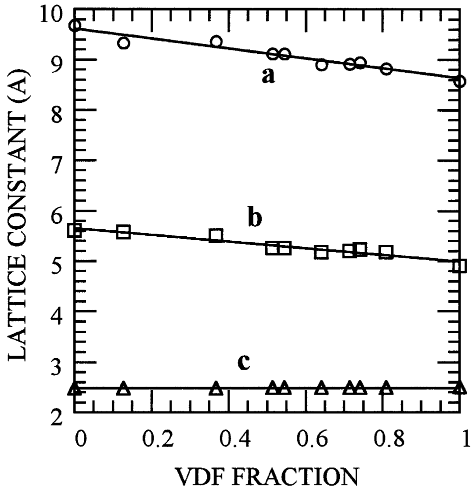

Fig. 9. Dependence of the three lattice constants on the VDF fraction [4,14,15].

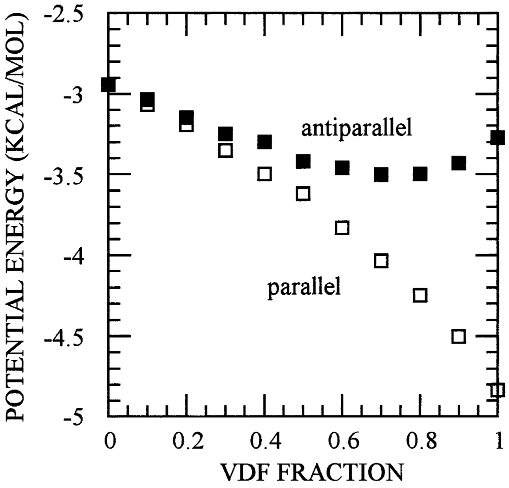

Fig. 10. Intermolecular potential energy calculated as a function of the VDF fraction when the VDF fraction dependence of the lattice constant is taken into account.

5. Discussion

Fig. 8 shows the VDF fraction dependence of the intermolecular interaction. The interaction energy for the parallel configuration decreases with an increase in the VDF fraction, but for the antiparallel configuration it increases. The variation in interaction energy for the parallel configuration was larger than that for the antiparallel. This result was obtained by using the lattice constants of PVDF [15] and neglecting their VDF fraction dependence. Fig. 9 shows the VDF fraction dependence of the lattice constants obtained experimentally [4,14,15].

Fig. 10 shows the revised figure for the VDF fraction dependence of the intermolecular interaction, taking into consideration the VDF fraction dependence of the lattice constant that was reproduced by the fitting line in Fig. 9. The variation in interaction energy increases for both parallel and antiparallel configurations, and the interaction energy for the antiparallel configuration initially decreases with the VDF fraction and reaches a minimum value near 70 mol% VDF fraction, after which it increases again.

The intermolecular interaction, V_0 in the statistical model described earlier, was defined as the difference between the interaction energies of parallel and antiparallel pairs. We then took up the difference in interaction energy, ΔU, between the two configurations in Fig. 7. Fig. 11 shows the VDF fraction dependence of ΔU. The ΔU shown by the open circles, are values when the VDF fraction dependence of the lattice constant is disregarded. ΔU changed in an almost linear fashion with the VDF fraction.

The molecular theoretical description, ΔU, of the interaction energy difference between parallel and antiparallel configurations in Fig. 7 is represented in terms of the intermolecular interaction, V_0, in the statistical model. The energy difference between parallel and antiparallel pairs in the statistical model is $2V_0$. The coordination

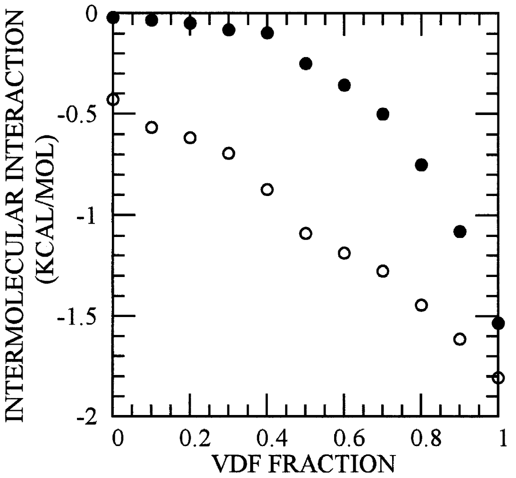

Fig. 11. The VDF fraction dependence of the intermolecular interaction calculated by summing Lennard-Jones potential between atoms. Values shown as solid circles were calculated taking the VDF fraction dependence of the lattice constants into account, values shown as open circles were calculated disregarding the VDF fraction dependence of the lattice constants.

number of the statistical model is 6. Assuming that a segment bearing an elementary process in the transition behavior is composed of n monomers we have:

$$\Delta U = 6(2V_0/n). \quad (12)$$

We assigned 2.4 kcal/mol to the interaction energy difference, δV_0, between V_0 at the VDF fraction 0.3 and that at 0.8, as shown in Fig. 6, and assigned 0.8 kcal/mol to $\delta(\Delta U)$ between them at the same VDF fractions, as shown in Fig. 11. We then found that n is about 36. A segment composed of 36 monomers in the planar zigzag structure of VDF type crystals should have a length of about 90 Å.

Since we previously assumed that the thickness of the crystal along the molecular axis is 1000 times the bond length, these VDF type crystals have much greater thickness than polyethylene crystal lamellae. The segment length, 90 Å, is about one-thirteenth of the thickness. In this model, after the smearing out effect, S, is selected, the critical transition temperature T_c becomes a unique function of V_0. So, to obtain a shorter or longer segment without a shift in T_c, we must select a smaller or larger S, respectively. Smaller S corresponds to thinner crystal lamellae or more a rigid molecule as it is derived from Eq. (3).

6. Conclusion

The copolymerization ratio dependence of the ferroelectric–paraelectric phase transition of copolymers of vinylidene fluoride and trifluoroethylene was reproduced using a simple model. Competition of the intermolecular and intramolecular interactions brings about the copolymerization ratio dependence of the phase transition. The VDF ratio dependence of the intermolecular interaction was determined by reproducing the phase diagram of the ferroelectric polymers. The VDF ratio dependence of the intramolecular interaction was assumed to be consistent with experimental results and theory. The intermolecular interaction strength shows a quadratic dependence on the VDF fraction and can be understood on the hypothesis that the behavior of the system was mainly controlled by the interaction between VDF monomers. The intermolecular interaction was also directly estimated by summing the Lennard-Jones potentials between all constituent atoms. Correspondence between the result obtained by reproduction of the phase transition behavior and that obtained directly gave 90 Å as the segment length of the phase transition behavior, although further work is needed for precise estimation of the segment length.

Acknowledgments

This work was supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan, No. 12650875.

References

[1] Ikeda S, Suda H. Phys Rev E 1997;56:3231.
[2] Koga K, Ohigashi H. J Appl Phys 1986;59:2142.
[3] Farmer BL, Hoppfinger AJ, Lando JB. J Appl Phys 1972;43:4293.
[4] Tashiro K, Kobayashi K, Chatani Y, Tadokoro H. Ferroelectrics 1984;57:297.
[5] Zhang R, Taylor PL. J Appl Phys 1993;73:1395.
[6] Jimbo M, Fukada T, Takeda H, Suzuki F, Horino K, Koyama K, Ikeda S, Wada Y. J Polym Sci, Polym Phys Ed 1986;24:909.
[7] Furukawa T, Matsuzaki H, Shiina M, Tajitsu Y. Jpn J Appl Phys 1985;24:L661.
[8] Tajitsu Y, Masuda T, Furukawa T. Jpn J Appl Phys 1987;26:1749.
[9] Sekimura T, Ikeda S. Rep Prog Polym Phys Jpn 1992;33:363.
[10] Tashiro K, Takano K, Kobayashi M, Chatani Y, Tadokoro H. Polymer 1981;22:1312.
[11] Davis GT, Furukawa T, Lovinger AJ, Broadhurst MG. Macromolecules 1982;15:329.
[12] Peterlin A, Fischer EW. Z Phys 1960;159:272.
[13] Al-Jishi R, Taylor PL. J Appl Phys 1985;57:897.
[14] Ohigashi H, Akama S, Koga K. Jpn J Appl Phys 1988;27:2146.
[15] Hasegawa R, Kobayashi M, Tadokoro H. Polym J 1972;3:591.