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Kinetics of the Ferroelectric−Paraelectric Transition of Copolymers of Vinylidene Fluoride and Trifluoroethylene: The Intermediate State during the Transition and the Effect of Critical Fluctuation on the Kinetics

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ABSTRACT: The kinetics of the phase transition between the ferroelectric and paraelectric phase in copolymers of vinylidene fluoride and trifluoroethylene was studied by measuring the time development of the dielectric permittivity during the phase transition with a temperature jump. It was found that the transition proceeds with several steps. In the paraelectric-to-ferroelectric transition, the fluctuation is enhanced at first and then the structural transition follows. The paraelectric phase transforms to the ferroelectric phase via an intermediate state, which is a quasi-stable paraelectric state with enhanced dipole fluctuation. At larger supercooling, the direct transition from paraelectric to ferroelectric phase also occurs. In the ferroelectric-to-paraelectric transition, the main process of transition is followed by a relaxation process. The nature of the intermediate state and the effect of critical fluctuation on the transition kinetics are discussed.

Introduction

Copolymers of vinylidene fluoride and trifluoroethylene, VDF/TrFE, have a solid-to-solid transition between ferroelectric and paraelectric phases. In the ferroelectric phase, a chain takes an all-trans conformation and packs parallel, resulting in a spontaneous polarization. In the paraelectric phase, a chain takes the conformation of a statistical mixture of trans and gauche, and therefore dipoles cancel out. On this transition there is a vast amount of studies of structural change, thermal properties, dielectric anomaly, molecular dynamics, etc.[1−3] Thus, the properties of each phase are considerably well-known. However, there were very few studies on the kinetics of transition, i.e., how the transition proceeds.

In the previous paper,[4] we reported the kinetics of the transition studied by the time development of permittivity on an application of a temperature jump. The permittivity changes with time, showing a characteristic time, and we call it the transition time. We determined the transition time as a function of temperature and discussed the transition mechanism on the basis of the nucleation and growth model that is similar to the crystallization kinetics.

It is well established that the transition is of the first order, not very far from the second-order transition.[5−7] That is, the lattice constant changes discontinuously at the transition temperature, and there exists latent heat as well as the temperature hysteresis, while the dielectric constant shows an anomaly and the relaxation time shows a slight slowing down at the transition temperature.[8] It indicates that some cooperative fluctuation is induced near the transition temperature. Such critical fluctuation may have a significant importance on the transition nature. Therefore, studying the effect of critical fluctuation on the transition kinetics is very interesting. In this paper, we report the dependence of the transition kinetics on the temperature before the temperature jump and discuss the effect of critical fluctuation on the transition behavior. We also discuss the nature of the intermediate state that was found to appear during the transition process.

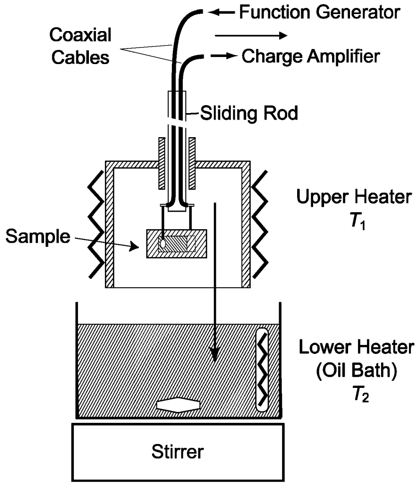

Figure 1. Schematic drawing of the apparatus. The sample can be moved into the oil bath with the sliding rod.

Experimental Section

Used are copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) of VDF content of 59 and 75 mol % supplied by Daikin Industries, Ltd. (Japan). We designate them as VDF/TrFE(59/41) and VDF/TrFE(75/25). They were cast from methyl ethyl ketone solution to form films of ca. 20 μm in thickness. After annealed at 145 °C for 1 h, gold was evaporated on both surfaces as electrodes.

The measuring apparatus is illustrated in Figure 1 and is the same as in the previous report.[4] A sample kept at temperature T_1 was dropped quickly in the oil bath of temperature T_2. Keeping applying a sinusoidal voltage of 1 kHz to the sample and measuring waveforms of the charge

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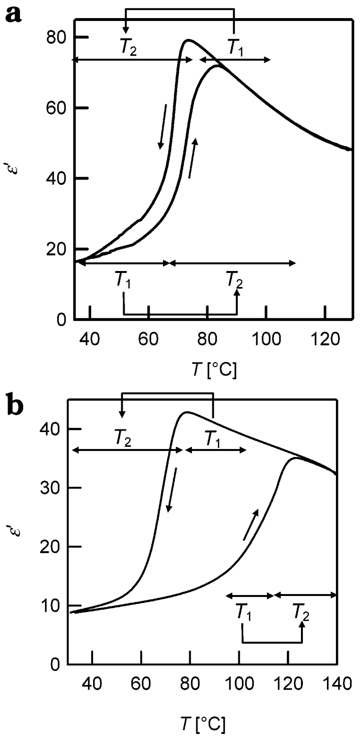

Figure 2. Temperature dispersion of the dielectric permittivity of (a) VDF/TrFE(59/41) and (b) VDF/TrFE(75/25). The ranges of T_1 and T_2 are indicated.

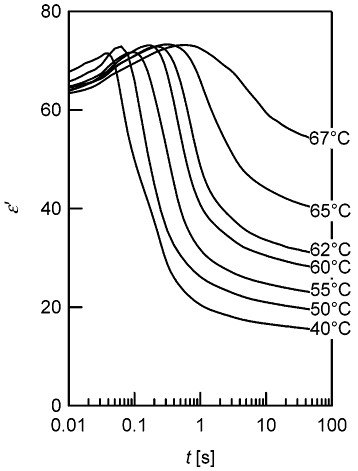

Figure 3. Time development of dielectric permittivity at transition from paraelectric to ferroelectric phase of VDF/TrFE(59/41). T_1 = 88 °C and T_2's are indicated in the figure.

response continuously by an A/D converter AT-MIO-16DE-10 (National Instruments Corp.) at a sampling interval of 0.1 ms, we calculated the permittivity repeatedly at every 1 ms and obtained the time development of permittivity associated with the temperature jump.

We measured the time development of the permittivity with various T_1 and T_2. The ranges of adopted T_1 and T_2 are illustrated with the temperature dispersions of the permittivity in parts a and b of Figure 2 for VDF/TrFE(59/41) and (75/25), respectively.

Results and Discussion

The permittivity seems to change from a value at T_1 to the eventual one at T_2 in two steps. Figure 3 shows the time development of permittivity in transition from the paraelectric to ferroelectric phase at various T_2 with T_1 = 88 °C for VDF/TrFE(59/41). In the process of the transition, the permittivity once increases from the value at T_1 and then decreases to the eventual value corresponding to T_2. VDF/TrFE(75/25) shows similar results as shown in Figure 4. For the transition from the ferroelectric to paraelectric phase, the permittivity once increases to a larger value than the eventual permittivity and then decreases as shown in Figure 5 and Figure 6 for VDF/TrFE(59/41) and (75/25). In the previous report,[4] we analyzed the transition kinetics by assuming the time constant of the most prominent process as the transition time: i.e., for transition from the paraelectric to ferroelectric phase, the second process is the phase transition process, while for the transition from the ferroelectric to paraelectric phase, the first process is the phase transition process. We succeeded in treating the transition kinetics as the nucleation and growth process. However, the whole transition process is composed of several steps, and there exists some intermediate state during the transition. Therefore, we tried to separate the processes as described below.

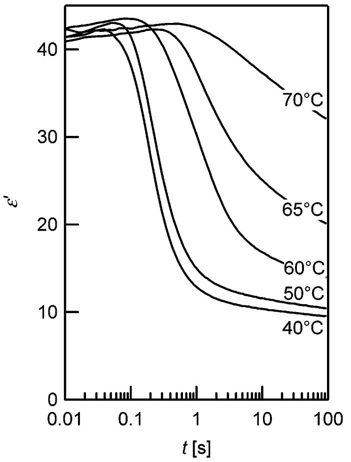

Figure 4. Time development of dielectric permittivity at transition from the paraelectric to ferroelectric phase of VDF/TrFE(75/25). T_1 = 80 °C and T_2's are indicated in the figure.

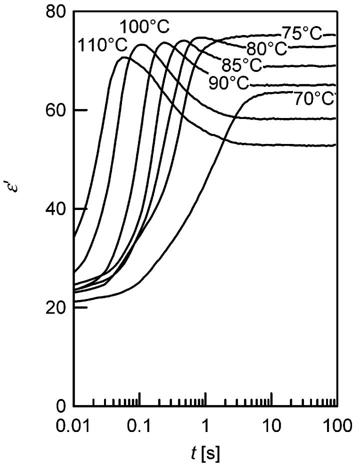

Figure 5. Time development of dielectric permittivity at transition from the ferroelectric to paraelectric phase of VDF/TrFE(59/41). T_1 = 50 °C and T_2's are indicated in the figure.

Calculation. The development of phase transition can be treated by the Avrami equation.[9] For the case of phase transition in one step, the fraction of transformed region ϕ at time t can be approximated by $\phi = 1 - \exp[-(t/\tau)^{\gamma}]$, where τ is the transition time and γ is a parameter that depends on the nucleation mechanism

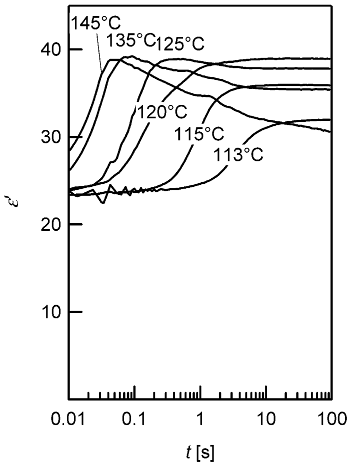

Figure 6. Time development of dielectric permittivity at transition from the ferroelectric to paraelectric phase of VDF/TrFE(75/25). $T_1 = 105$ °C and T_2's are indicated in the figure.

and the dimensionality of the growth of transformed regions. This means that the fraction of the region that is not transformed decreases with time as $\exp[-(t/\tau)^{\gamma}]$. In the case of the ferroelectric–paraelectric transition in VDF/TrFE, we must treat the transition kinetics as two sequential processes. Thus, as an expansion of the Avrami treatment, we estimated the time development of the fraction ϕ_1, ϕ_2, and ϕ_3 of original, intermediate, and final states, respectively, as functions of time t by approximating as

$$\begin{cases} \phi_1 = \exp[-(t/\tau_1)^{\gamma_1}] \\ \phi_2 = \exp[-(t/\tau_2)^{\gamma_2}] - \exp[-(t/\tau_1)^{\gamma_1}] \\ \phi_3 = 1 - \exp[-(t/\tau_2)^{\gamma_2}] \end{cases} \tag{1}$$

where τ_1 and τ_2 are the characteristic times of the first and second process and γ_1 and γ_2 are parameters depending on the kinetics of each process.

The apparent permittivity of the sample that is composed of three components with permittivity ϵ_i and fraction ϕ_i with $i = 1-3$ depends on the spatial distribution of each component. Here, we neglected the contribution of amorphous regions for simplicity because the degree of crystallinity of the copolymers is very high. As the new phase may appear stochastically in the original phase, the most natural picture of the distribution may be the random dispersion of spherical transformed regions in the original phase. In such case, the apparent permittivity ϵ is expressed as

$$\epsilon = \frac{2\epsilon_1 + \epsilon_m - 2\phi_m(\epsilon_1 - \epsilon_m)}{2\epsilon_1 + \epsilon_m + \phi_m(\epsilon_1 - \epsilon_m)}\epsilon_1 \tag{2}$$

where ϕ_m is the fraction of transformed regions and ϵ_1 and ϵ_m are the permittivity of original and transformed regions. Here, the *transformed regions* include those regions that have already experienced the second process, and thus $\phi_m = \phi_2 + \phi_3$. ϵ_m is the apparent permittivity of the *transformed regions* and is given by formula 2 with ϵ_1 and ϵ_m replaced by ϵ_2 and ϵ_3 and $\phi_m = \phi_3/(\phi_2 + \phi_3)$. Figures 7 and 8 illustrate examples of the fitting to the transition processes of ferroelectric-to-paraelectric and paraelectric-to-ferroelectric, respectively.

Paraelectric-to-Ferroelectric Transition. The experimental results of the paraelectric-to-ferroelectric transition are well fitted by eqs 1 and 2, except for the gradual decrease continuing for several decades following the major decrease as exemplified in Figure 8. There exists a very slow process in the transition from the paraelectric to ferroelectric phase, which we will discuss later. First of all, we discuss the first two processes with estimated kinetic parameters obtained by fitting.

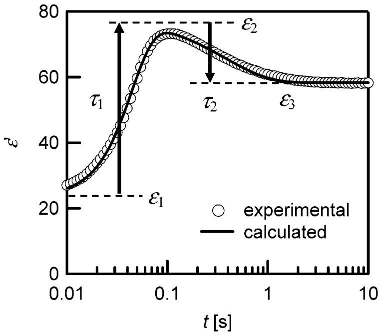

Figure 7. Definition of fitting parameters and an example of curve fitting to the time development of permittivity from the ferroelectric to paraelectric phase.

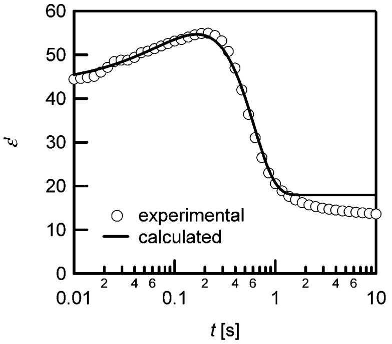

Figure 8. An example of fitting to the time development of permittivity from the paraelectric to ferroelectric phase.

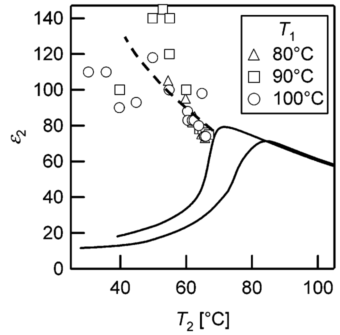

Figure 9. Permittivity of the intermediate state ϵ_2 plotted against T_2 with various T_1 in the process of transition from the paraelectric to ferroelectric phase of VDF/TrFE(59/41). The solid curve is the temperature dispersion of permittivity.

The kinetic parameters γ_1 and γ_2 are scattering but take values near unity for all results. This suggests that the transition proceeds via one-dimensional growth with heterogeneous nucleation or the process is controlled by the nucleation in each crystallite. However, the discussion on these parameters is not very conclusive at this stage. Figure 9 shows the dependence of ϵ_2 on T_2 for various T_1 for VDF/TrFE(59/41). The results for VDF/TrFE(75/25) are essentially the same. The dielectric permittivity of the intermediate state ϵ_2 takes a large value that can be regarded as an extrapolation of the Curie–Weiss law of the permittivity of the paraelectric phase to T_2. As shown in Figure 10, the characteristic

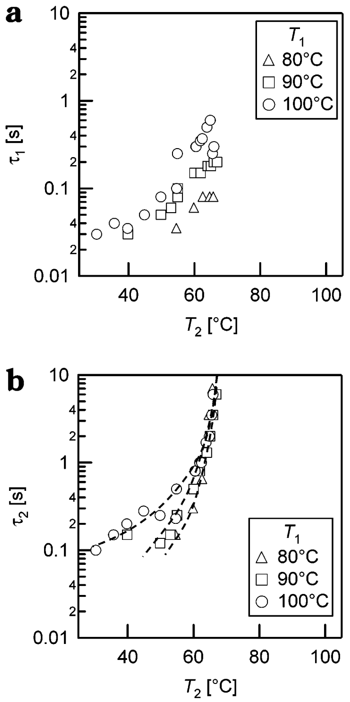

Figure 10. Time constants (a) τ_1 and (b) τ_2 plotted against T_2 with various T_1 in the process of transition from the paraelectric to ferroelectric phase of VDF/TrFE(59/41).

time τ_1 depends on temperature T_2 only weakly, while τ_2 depends on T_2 very strongly, and it tends to diverge to infinity as the supercooling becomes small. It is the second process that we can treat as a nucleation-and-growth process of ferroelectric phase in the paraelectric phase as we reported previously.[4] The transition time depends on the temperature T_2 as

$$\tau_2 \sim \exp\left(\frac{A}{T_2(T_c^0 - T_2)^2}\right) \tag{3}$$

where T_c^0 is the equilibrium transition temperature and A is a constant, and it diverges as T_2 approaches T_c^0.

Now, what is the first process? As the permittivity of the intermediate state corresponds to the extrapolation of the paraelectric phase to the lower temperature, it is plausible that the intermediate state is the paraelectric phase that is quasi-stable at T_2. The first process is, then, the development of critical fluctuation toward the state corresponding to T_2. Such regions appear stochastically in the paraelectric phase and increase on approach to the critical point that may exist below the observed transition temperature as described by the phenomenological theory for the case of the first-order transition.[10] As the formation of the ferroelectric phase requires a nucleation of regularly arranged region of the all-trans chain oriented in the same direction, the transition takes some time after the temperature jump, and thus the quasi-stable state can exist for a while.

We can see in Figure 10b that the transition time τ_2 depends on T_1. If the fluctuation reaches totally the state corresponding to T_2 before the transition occurs, we cannot expect such a T_1 dependence. However, the T_1 dependence is only apparent for relatively low T_2 where the supercooling is very large, and the transition occurs very quickly. In such case, the transition also occurs directly from the paraelectric phase corresponding to the state at T_1 in addition to the sequence via the intermediate state, and this process dominates at larger supercooling. The dependence of τ_2 on T_1, therefore, can be regarded as reflecting the state of fluctuation in the paraelectric phase at T_1: The lower T_1 becomes, the faster the transition occurs. Because the critical fluctuation is more prominent at lower T_1, the nucleation rate of the ferroelectric phase is enhanced, and the transition process becomes faster.

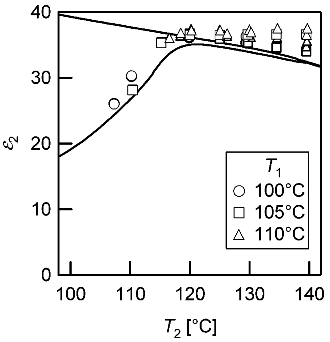

Figure 11. Permittivity of the intermediate state ϵ_2 plotted against T_2 with various T_1 in the process of transition from the ferroelectric to paraelectric phase of VDF/TrFE(75/25). The solid curve is the temperature dispersion of permittivity.

In addition to the two processes discussed above, there exists a very slow decrease in permittivity in the transition from the paraelectric to ferroelectric phase. One possible mechanism of this slow process is that there exist a lot of defects in the as-transformed ferroelectric phase resulting in larger permittivity, and the slow process is due to the gradual dissolution of such defects with time. With the progress of transition into the ferroelectric phase, the cooperativity in the crystal lowers the mobility of chains, and defective regions such as the defect of chain conformation, the domain wall, etc., are left behind. The removal of such defects needs a long time and is observed as the slow decrease in permittivity continuing for more than 1 day. Thus, the whole transition process in the paraelectric-to-ferroelectric transition can be summarized as

$$\text{para}(T_1) \xrightarrow[\tau_1]{} \text{para}(T_2) \xrightarrow[\tau_2]{} \text{defective ferro}(T_2) \rightarrow \text{ferro}(T_2)$$

At larger supercooling, the sequence

$$\text{para}(T_1) \rightarrow \text{defective ferro}(T_2) \rightarrow \text{ferro}(T_2)$$

also occurs.

Ferroelectric-to-Paraelectric Transition. For the case of the transition from ferroelectric to paraelectric phase, we can fit the whole process essentially by eqs 1 and 2. The first process is the large increase in the permittivity, and the second one is the gradual decrease to the equilibrium state at T_2. The kinetic parameters γ_1 and γ_2 are scattering but take values near unity being similar to the case of the paraelectric-to-ferroelectric transition. The permittivity of the intermediate state ϵ_2 is plotted against T_2 in Figure 11 for VDF/TrFE(75/25). The results for VDF/TrFE(59/41) are essentially the same. In contrast to the transition from the paraelectric to ferroelectric phase, the permittivity of the intermediate state is not the extrapolation of the ferroelectric phase. Figure 12 shows the T_2 dependence of the characteristic times τ_1 and τ_2. The kinetics of the first

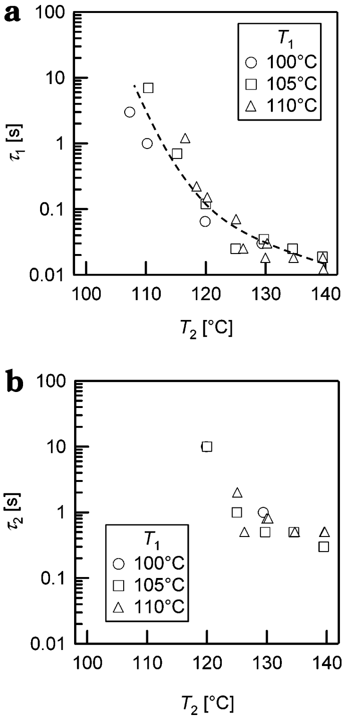

Figure 12. Time constants (a) τ_1 and (b) τ_2 plotted against T_2 with various T_1 in the process of transition from the paraelectric to ferroelectric phase of VDF/TrFE(75/25).

process has a strong dependence on the superheating and obeys a kinetic relation similar to eq 3. These results indicate that the first process is the phase transition process in the case of the ferroelectric-to-paraelectric transition, being consistent with the assumption in the previous paper.[4] The second process has a relatively small change in permittivity, and its characteristic time depends on T_2 only weakly. It may be some relaxation process such as the dissolution of remaining component of the all-trans region. Thus, the transition can be depicted as

$$\mathrm{ferro}(T_1) \xrightarrow[\tau_1]{} \text{defective para}(T_2) \xrightarrow[\tau_2]{} \mathrm{para}(T_2)$$

The T_1 dependence is not apparent in the case of the ferroelectric-to-paraelectric transition. The effect of fluctuation in the ferroelectric phase on the transition kinetics may not be large because the nucleation of disordered phase can easily occur at any place such as the boundary of crystallites.

Conclusion

The kinetics of the phase transition between the ferroelectric and paraelectric phase in VDF/TrFE copolymers was studied by the time development of the permittivity with a temperature jump. The transition process from paraelectric to ferroelectric phase was separated into three steps, which can be considered as the process of the enhancement of fluctuation, the main process of structural transition and the slow process of eliminating defects. At larger supercooling, the direct transition from the paraelectric to ferroelectric phase occurs. In this case, the transition velocity depends on the temperature before the temperature jump. This can be explained that in highly fluctuating regions the ferroelectric phase is easy to nucleate. In the case of transition from ferroelectric to paraelectric phase, the transition kinetics is not dependent on the temperature before the temperature jump. It can be explained that the nucleation of paraelectric domain can easily occur at any place, and the influence of fluctuation in the ferroelectric phase is not very large for the transition kinetics.

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