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Proton Spin Lattice Relaxation in Vinylidene Fluoride/Trifluoroethylene Copolymers II. Effects of Vinylidene Fluoride Content upon Spin Relaxation Processes

Fumiaki ISHII and Akira ODAJIMA

Department of Applied Physics, Faculty of Engineering,
Hokkaido University, Sapporo 060, Japan

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ABSTRACT: In the proton spin lattice relaxation time T_1 measurements on VDF/TrFE copolymers with the VDF contents of 52 and 65 mol%, three kinds of spin lattice relaxation processes were observed below the Curie temperature T_c, around T_c and in a certain temperature region above T_c. They were compared with those of P(VDF$_{72}$/TrFE$_{28}$). The thermal hysteresis of T_1 against temperature for each relaxation process became smaller in order of the VDF contents of 72, 65, and 52 mol%.

The T_1 in the paraelectric phase for each copolymer was analyzed, on the basis of Bloembergen's theory, in terms of the non-exponential correlation function which describes a one-dimensional diffusion motion of conformational defects along the chain. The activation energy of the 1-D diffusion motion was about 8.5 kcal mol^{-1} which did not depend on the VDF content. The $1/T_1$ and the correlation time of the 1-D diffusion motion for each copolymer were converted, respectively, to those of P(VDF$_{72}$/TrFE$_{28}$) with the scaling factors of ξ^{-2} and ξ^{-4}, in which the ξ is the ratio of the VDF content (mol%) to 72 mol%.

KEY WORDS Vinylidene Fluoride / Trifluoroethylene Copolymer / Vinylidene Fluoride Content / Spin Lattice Relaxation Time / Thermal Hysteresis / Paraelectric Phase / 1-D Diffusion Motion / Conformational Defects / Scaling Factor /

It is well known that the copolymer of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) exhibits the ferroelectric phase transition, which strongly depends on the VDF content, and that the thermal hysteresis of the transition appears when the VDF content exceeds 55 mol%. The thermal hysteresis may be associated with a *trans–gauche* energy difference $\Delta U(=U_{TT}-U_{TG})$ of polymer chain. It has been elucidated by Tashiro *et al.*[1] from the infrared absorbances of *trans* and *gauche* bonds in the paraelectric phase that as the VDF content increases the ΔU changes its sign from negative to positive, this is, the conformational stability of the chain changes from *trans* to *gauche*. Odajima[2] corroborated by means of a modified Ising Model that, for the positive energy difference of the *trans* form to the *gauche* form, the phase transition is of a first order and its thermal hysteresis also becomes larger. In Part I of this series,[3] three kinds of the spin-lattice relaxation processes have been investigated in the drawn film of P(VDF$_{72}$/TrFE$_{28}$), which were named as β, α_t, and α_b' in order of increasing temperature of their appearance. The β and α_t relaxations are respectively associated with the motion of the chain backbone in partially crystalline regions and the ferroelectric phase transition. The nuclear spin-lattice relaxation time T_1 for α_b' becomes larger with increasing the resonance angular frequency ω, temperature T and the alignment angle γ between the magnetic field H_0 and the drawn direction of the film. The formula for T_1 in an isolated spin pair modulated by a one-dimentional (1-D) diffusion motion of the conformational defects was derived from Bloembergen's theory,[4] in terms of the non-exponential correlation function obtained by Hunt and Powles.[5] Existence of the 1-D diffusion motion in the paraelectric phase[6] was confirmed from the reasonable agreement between theory and the experimental results.

The purpose of this paper is to report further the T_1 measurements on the drawn films of P($VDF_{52}/TrFE_{48}$) and P($VDF_{65}/TrFE_{35}$), examining how the VDF content affects three kinds of spin lattice relaxation processes, which are β, α_t, and α_b' described in Part I.[3] The T_1's for the α_b' relaxation in both copolymers are analyzed, on the basis of Bloembergen's theory,[4] in terms of the non-exponential correlation function, and compared with the results of P($VDF_{72}/TrFE_{28}$).[3] Then, we will show that the $1/T_1$ and the correlation time of the local field modulated by the 1-D diffusion motion in each copolymer are converted to those in P($VDF_{72}/TrFE_{28}$) by the scaling factors of ξ^{-2} and ξ^{-4}, respectively, in which ξ is the ratio of the VDF content x ($x=52$ or 65 mol%) to that of 72 mol%.

EXPERIMENTAL

The samples used were the $VDF_x/TrFE_{100-x}$ copolymers with the VDF contents of $x=52$, and 65 mol%, which were supplied by the Daikin Kogyo Co., Ltd. The films of these copolymers were prepared by slowly casting from 2-butanone solutions under atmosphere at room temperature and then were drawn × 6 uniaxially. The drawn films of P($VDF_{52}/TrFE_{48}$) and P($VDF_{65}/TrFE_{35}$) were annealed at 130°C for 20 h and 9 h while pressing them between glass plates. Then, their final drawn ratios were 4 for P($VDF_{52}/TrFE_{48}$) and 4.5 for P($VDF_{65}/TrFE_{35}$).

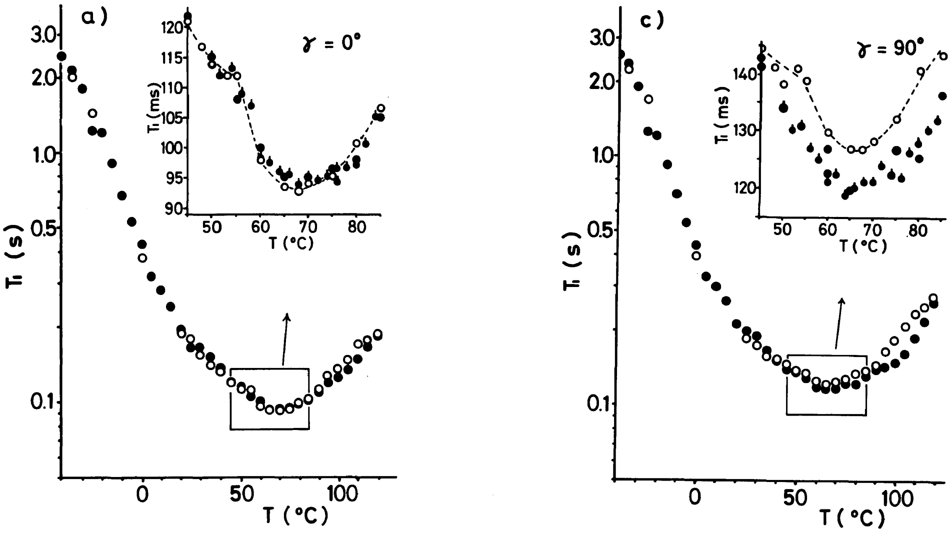
The T_1's in both copolymers were measured for $\gamma=0$, 45 and 90° by using a NMR pulse spectrometer, operating at 20 and 90 MHz over a temperature range from -23 and 120°C. The processes of the temperature rise from -23 to 120°C and the fall from 120 to -23°C are taken as the arrow signs of ↑ and ↓, respectively.

A pulse NMR spectrometer, procedures of operation and data reduction of T_1 have been described elsewhere.[3]

RESULTS

Figures 1a, b, and c show the ln T_1 as a function of T for $\gamma=0$, 45, and 90° in P($VDF_{52}/TrFE_{48}$). The filled (–●–) and unfilled (–○–) circles are the values of T_1 in the ↑- and ↓-processes, respectively. The T_1 *vs.* T curves for $\gamma=0$, 45, and 90° minimize at about 68°C in the ↑- and ↓-processes and indicate the concave curves over the whole temperatures. The P($VDF_{52}/TrFE_{48}$) does not almost exhibits an thermal hysteresis of the T_1 in both ↑- and ↓-processes. In each T_1 *vs.* T curve in the ↓-process, a discontinuity is observed evidently in the temperature region between 55 and 60°C (↓), comparing with those in the ↑-process. Figure 2 shows the γ-dependence of the ln T_1 *vs.* T^{-1} curve in P($VDF_{52}/TrFE_{48}$) in the ↓-process. For each orientation, a linear relationship can be observed in the temperature range from 95 to 120°C in ↓-process. In the temperature region between 120 and 40°C (↓), the value of T_1 becomes larger in order of $\gamma=0$, 45, and 90°. The ln T_1 *vs.* T^{-1} curves for $\gamma=45$ and 90° intersect each other at 35°C.

It is considered that three kinds of the spin-lattice relaxations take place in the three temperature ranges of 30 to 50°C, 60 to 95°C, and 95 to 120°C in both ↑- and ↓-processes. These relaxation processes are referred to as β, α_t, and α_b' in order of increasing temperature in a similar way to P($VDF_{72}/TrFE_{28}$).[3] In Table I, the temperature ranges of the β, α_t, and α_b' relaxations in the ↑- and ↓-processes are summarized.



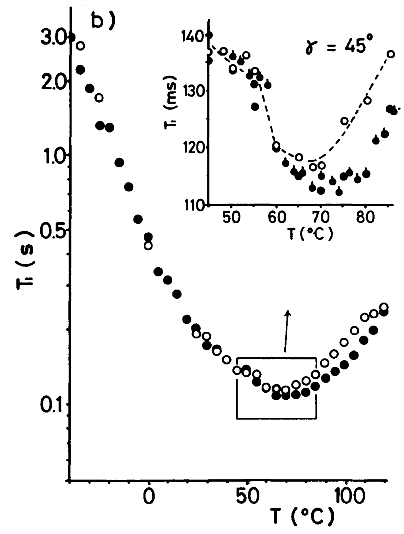


Figure 1. Temperature dependences of T_1 for P(VDF$_{52}$/TrFE$_{48}$): (a) $\gamma=0°$, (b) $\gamma=45°$, and (c) $\gamma=90°$. The filled and unfilled circles indicate T_1 in the ↑- and ↓-processes, respectively. The insets show the behavior of T_1 between 45 and 95°C in the ↑-process (●, first run; ♦, second run) and in the ↓-process (—○—).

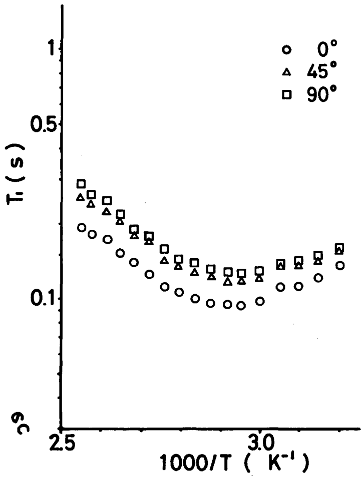
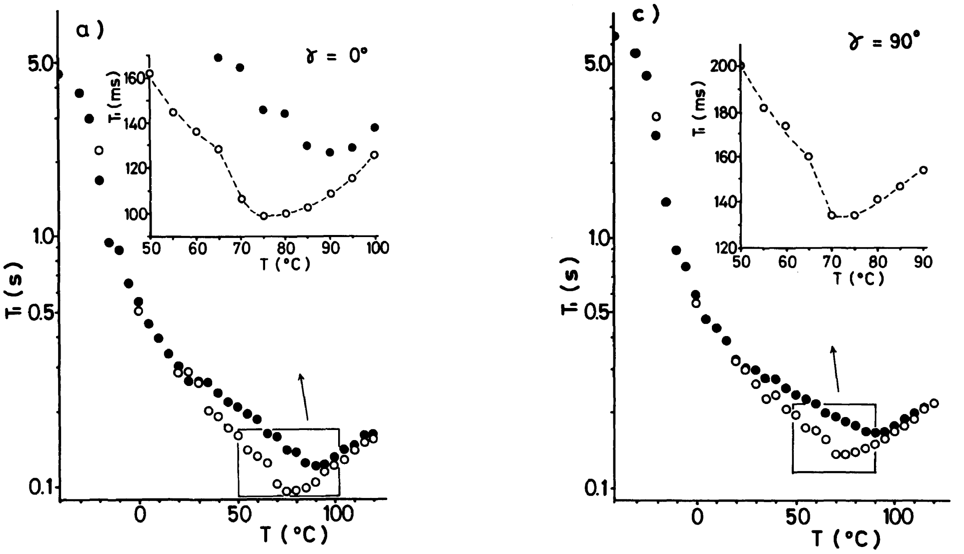


Figure 2. Plots of T_1 against reciprocal temperature for P(VDF$_{52}$/TrFE$_{48}$) in the cooling process. The filled circles and the unfilled triangles and circles indicate T_1 for $\gamma=0$, 45, and 90°, respectively.

Figures 3a, b, and c show the ln T_1 as a function of T in P(VDF$_{65}$/TrFE$_{35}$) for $\gamma=0$, 45, and 90°. In the ↑-process, they indicate the concave curve over the whole temperatures and minimize at about 89°C (↑). The concave curve for each γ may be constructed from three kinds of the relaxation processes which are referred to as β (↑), α_t (↑), and α_b' (↑). No β (↑) relaxation can be separated from the α_t (↑) relaxation in contrast with that in P(VDF$_{72}$/TrFE$_{28}$).[3] Therefore, the temperature region of the relaxation was determined as below 79°C where a discontinuous line narrowing of the broad width was observed in the line width[8] measurements. In the ↓-process, the T_1 value for each angle γ is lower than that



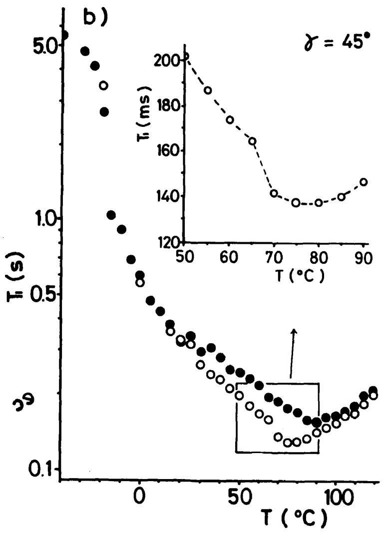


Figure 3. Temperature dependences of T_1 for P(VDF$_{65}$/TrFE$_{35}$): (a) $\gamma=0°$, (b) $\gamma=45°$, and (c) $\gamma=90°$. The filled and unfilled circles indicate T_1 in the ↑- and ↓-processes. The insets show the behavior of T_1 near the transition temperature in the ↑-process (●) and in the ↓-process (--○--).

Table I. Classification of spin relaxation processes of P(VDF$_{52}$/TrFE$_{48}$)

↑-Process		↓-Process	
Relaxation process	Temperature range °C	Relaxation process	Temperature range °C
β	30— 55[a]	β	30— 55[a]
α_t	60— 95	α_t	60— 95
α_b'	95—120[b]	α_b'	95—120[b]

[a] Assumed that the temperature region of the β relaxation is below 55°C where the value of T_1 varies discontinuously.

[b] Determined from the linearity of the $\ln T_1$ against reciprocal temperature in the paraelectric phase.

corresponding in the ↑-process. The value of the T_1 for each angle γ decreases gradually from 120°C and is minimal at 75°C (↓). After the T_1 increases abruptly between 70 and 65°C (↓), it increases slowly and at 30°C returns to that in the ↑-process. A discontinuity is observed in the T_1 *vs.* T curve for each angle γ between 65 and 70°C (↓) more clearly than that of P(VDF$_{52}$/TrFE$_{48}$). Figure 4 shows the T_1 ploted against T^{-1} in P(VDF$_{65}$/TrFE$_{35}$) for $\gamma=0$, 45, and 90° in the ↓-process. T_1 increases in order of the angle $\gamma=0$, 45, and 90° between 120 and 70°C (↓), and in order of the angle $\gamma=0$, 90, and 45° below 65°C (↓). P(VDF$_{65}$/TrFE$_{35}$) also exhibits three kinds of spin-lattice relaxations in the ↓-process, that is, β (↓), α_t (↓), and α_b' (↓), which take place in the three

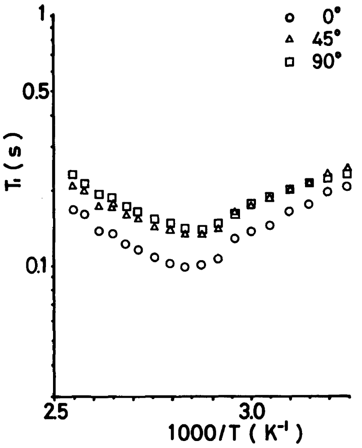


Figure 4. Plots of T_1 against reciprocal temperature for P(VDF$_{65}$/TrFE$_{35}$). The circles, triangles and squares indicate T_1 for $\gamma=0$, 45, and 90°, respectively.

Table II. Classification of spin relaxation processes of P(VDF$_{65}$/TrFE$_{35}$)

↑-Process		↓-Process	
Relaxation process	Temperature range °C	Relaxation process	Temperature range °C
β	30—79[a]	β	30—65[b]
α_t	85—100	α_t	70—95
α_b'	100—120[c]	α_b'	95—120[c]

[a] Assumed that since no the β (↑) relaxation can be separated from the α_t (↑) relaxation, the temperature region is below 79°C where a discontinuous line narrowing was observed in NMR line width measurement.[8]

[b] Determined that the temperature region of the β (↓) is below 65°C where the value of T_1 increases discontinuously.

[c] Determined from the linearity of the ln T_1 against reciprocal temperature in the paraelectric phase.

temperature ranges from 30 to 65°C (↓), 70 to 95°C (↓), and 95 to 120°C (↓), respectively. In Table II, the temperature ranges of the β, α_t, and α_b' relaxations in the ↑- and ↓-processes are summarized.

Figures 5a, b, and c show the ln T_1 *vs.* ln ω curves in P(VDF$_x$/TrFE$_{100-x}$) with the VDF contents of 52, 65, and 72 mol% at 110°C (↓). The T_1 *vs.* ln ω curves of P(VDF$_{72}$/TrFE$_{28}$) have been given in Part I of this series.[3] The circle, triangle and rectangle in each figure indicate the values of T_1 in the ↓-process for $\gamma=0$, 45, and 90°, respectively. T_1 for each copolymer becomes longer with increasing of ω and γ.

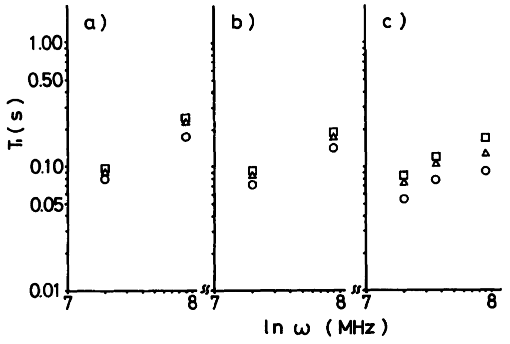


Figure 5. Plots of ln T_1 *vs.* ln ω at 110°C (↓) for three VDF/TrFE copolymers: (a) P(VDF$_{52}$/TrFE$_{48}$), (b) P(VDF$_{65}$/TrFE$_{35}$), and (c) P(VDF$_{72}$/TrFE$_{28}$). The circles, triangles and squares indicate T_1 for $\gamma=0$, 45, and 90°, respectively.

DISCUSSION

The Behavior of Spin-Lattice Relaxation Time T_1 near T_c

Thermal hysteresis of the T_1 *vs.* T curve becomes smaller in order of the VDF content from 72 to 52 mol%. In Table III, the temperatures of the T_1 minima, T_c (↑) and T_c (↓), in P(VDF$_x$/TrFE$_{100-x}$) with x of 53, 65, and 72 mol% are listed. The temperatures of the T_1 minima for P(VDF$_{72}$/TrFE$_{28}$) were determined in the previous paper.[3] Both T_c (↑) and T_c (↓) shift to lower temperature as the VDF content decreases. They agree approximately with the corresponding transition temperatures obtained from the dielectric[6] and DSC[6], and NMR line width[7,8] measurements. Therefore, the T_1 for the α_t-relaxation in each copolymer is dully minimul at T_c due to the ferroelectric phase transition. This dull minimum of the T_1 suggests that the critical slow-

Table III. The temperatures of T_1 minima for three VDF/TrFE copolymers with the VDF contents of 52, 65, and 72 mol% in the heating and cooling processes

	52/48		65/35		72/28	
	$T_c(\uparrow)$	$T_c(\downarrow)$	$T_c(\uparrow)$	$T_c(\downarrow)$	$T_c(\uparrow)$	$T_c(\downarrow)$
	°C	°C	°C	°C	°C	°C
T_1	68	68	90	75	115	79
ΔH[a]	63	63	89	70	116	75
DSC[b]	60	62	70	64	114	75
$1/\Delta\varepsilon$[b]	79	73	102	69	134	84

[a] Observed from the discontinuous narrowing of the NMR line width.[7,8]

[b] Observed from the minimum of the reciprocal dielectric strength $1/\Delta\varepsilon^6$ and the endotherm starting point on the DSC curve.[6]

ing down of the molecular motion due to polarization fluctuation near T_c is affected by a first order of the phase transition. The value of T_1 in the phase transition region becomes larger in order of VDF content $x=72$, 52, and 65 mol%. While, the dielectric relaxation strength $\Delta\varepsilon$ near T_c obtained from the dielectric measurements[6,9] increases in order of VDF content $x=72$, 52, and 65 mol%. It was previously[10] estimated from the values of T_1 and $\Delta\varepsilon$ at T_c for each copolymer that the correlation energy in the spatial variation of polarization due to the critical fluctuation becomes larger in order of VDF content $x=$ 72, 65, and 52 mol%. This means that the spatial inhomogeneity due to the polarization fluctuation is reflected in T_1 near T_c.

The β-relaxations for P(VDF$_{52}$/TrFE$_{48}$) and P(VDF$_{65}$/TrFE$_{35}$) appear below T_c in the ↑- and ↓-processes, respectively. The T_1 *vs.* T curve in each copolymer does not take the minimum value in the β relaxation region. While the minimization of T_1 for the relaxation was observed at 88°C in the heating process for P(VDF$_{72}$/TrFE$_{28}$) only.[3] This is attributed to the finding that the temperature of 88°C for the β-relaxation is higher than all T_c's, except the T_c (↑) in P(VDF$_{72}$/TrFE$_{28}$) as shown in Table II. The values of T_1 for the β relaxation become larger in order of the VDF content $x=72$, 52, and 65 mol%. The β relaxation may be due to the molecular motion of the chain backbone in partially crystalline regions.[6] The 1-D diffusion motion of conformational defects in the paraelectric phase.

In the previous papers,[3,7] the formular for T_1 of an isolated spin pair modulated by a one-dimensional (1-D) diffusion motion of conformational defects was given, at the high temperature limit, as follows:

$$\ln T_1 = -1/2 \ln \tau_D + 1/2 \ln \omega - \ln\{(1+2\sqrt{2}) + 6\cos^2\gamma + (1-2\sqrt{2})\cos^4\gamma\} - \ln A \qquad (1)$$

where $A = 9/128\ \gamma^4 \hbar^2 I(I+1) r^{-6}$ and $\omega = 2\pi f_r$. The τ_D is defined as

$$\tau_D = l_d^2/D \qquad (2)$$

where l_d is a mean distance between a given isolated spin pair and the nearest conformational defect and D is the diffusion coefficient. Inserting eq 2 into eq 1, T_1 is represented by

$$\frac{1}{T_1} = B\tau_D^{1/2} = B\frac{l_d}{\sqrt{D}} \qquad (3)$$

where

$$B = A^{-1}\omega^{-1/2}\{(1+2\sqrt{2}) + 6\cos^2\gamma + (1+2\sqrt{2})\cos^4\gamma\}$$

Assuming that τ_D is expressed by Arrhenius type, $\tau_D = \tau_0 \exp(\Delta E/RT)$, eq 1 becomes

$$\ln T_1 = \frac{1}{2}\left(\frac{\Delta E}{R}\right)\frac{1}{T} - \ln B \qquad (4)$$

where ΔE is an activation energy of the 1-D diffusion motion.

If each ln T_1 *vs.* ln ω curve in Figure 5 is linear, the slope of each line is determined from the experimental data by using the least square method. Table IV illustrates the

Table IV. The averaged slopes, '$\bar{a}$'s,' of $\ln T_1$ *vs.* $\ln \omega$ at 110°C (↓) for the VDF/TrFE copolymers with the VDF contents of 52, 65, and 72 mol%, and the averaged activation energy of the α_b' relaxation in each copolymer in the cooling process

VDF/mol%	52	65	72[a]
$\bar{a}$	0.58	0.49	0.50
ΔE/kcal mol^{-1}	8.7	8.7	8.2

[a] The values of $\bar{a}$ and ΔE for P(VDF$_{72}$/TrFE$_{28}$) were determined in Part I of this series.[3]

average slopes, $\bar{a}$'s for the copolymers with VDF contents of 52, 65, and 72 mol%. The $\bar{a}$-values for P(VDF$_{52}$/TrFE$_{48}$) and P(VDF$_{65}$/TrFE$_{35}$) are respectively 0.58 and 0.49, which are approximately equal the theoretical value 0.5 obtained from eq 1.

The plots of the $\ln T_1$ against T^{-1} for $\gamma=0$, 45, and 90° in each copolymer yield a straight line in the temperature range from 95 to 120°C (↓) as shown in Figures 2 and 4. The values of T_1 become longer in order of the $\gamma=0$, 45, and 90°. The averaged ratios of T_1's for $\gamma=45$ and 90° to that for $\gamma=0°$ in the temperature range are respectively 1.26 and 1.38 for P(VDF$_{52}$/TrFE$_{48}$), and 1.27 and 1.42 for P(VDF$_{65}$/TrFE$_{35}$). Comparing these ratios with the ratios of 1.28 and 1.41 for P(VDF$_{72}$/TrFE$_{28}$), we can see that these ratios of T_1's in the copolymers are almost independent of the VDF content. The experimental values of these ratios agree qualitatively with the theoretical ratios of 1.26 and 2.1, which is calculated from eq 1.

Using eq 4 and the values of the slope of $\ln T_1$ *vs.* T^{-1} in each copolymer obtained for $\gamma=0$, 45, and 90°, the activation energy of the 1-D diffusion motion is calculated. The averaged activation energies for P(VDF$_{52}$/TrFE$_{48}$) and P(VDF$_{65}$/TrFE$_{35}$) are listed in Table IV together with that in P(VDF$_{72}$/TrFE$_{28}$). The activation energy of about 8.5 kcal/mol is almost independent of the VDF content. Therefore, the existence of a 1-D diffusion motion of the conformational defects in the paraelectric phase is confirmed from the reasonable agreement between the theoretical and the experimental relations of T_1 to ω, γ and T^{-1}.

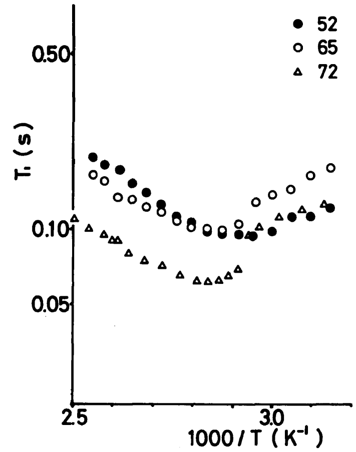


Figure 6. The effect of the VDF content on the T_1 behavior of the VDF/TrFE copolymer in the cooling process. P(VDF$_{52}$/TrFE$_{48}$), P(VDF$_{65}$/TrFE$_{35}$), and P(VDF$_{72}$/TrFE$_{28}$).

Influence of the VDF Content on a One-Dimensional Diffusion Motion of the Conformational Defect

Figure 6 shows the $\ln T_1$ plotted against T^{-1} in P(VDF$_x$/TrFE$_{100-x}$) with x of 52, 65, and 72 mol% for $\gamma=0°$. In the high temperature region in the paraelectric phase, the T_1 becomes longer as the VDF content decreases. T_1's for $\gamma=45$ and 90° also depend on the VDF content in a similar way to that for $\gamma=0°$. Let us express the observed $(1/T_1)_{\text{ob}}$ at 110°C (↓) and the VDF content 'x' in P-(VDF$_x$/TrFE$_{100-x}$) as values relative to corresponding those in P(VDF$_{72}$/TrFE$_{28}$), which are referred to as $(1/T_1)_{72}$ and 72, respectively. Then, two parameters, $P_{\text{ob}}(\gamma)$ and ξ are defined by the following equations

$$P_{\text{ob}}(\gamma)=\frac{\left(\dfrac{1}{T_1}\right)_{\text{ob}}(\gamma)}{\left(\dfrac{1}{T_1}\right)_{72}(\gamma)} \tag{5a}$$

Table V. Scaling factors $\bar{P}_{ob}$ and ξ^2 of $(1/T_1)$'s for the VDF/TrFE copolymers with the VDF contents of 52, 65 and 72 mol% to that for P(VDF_{72}/$TrFE_{28}$) at 110°C in the cooling process

VDF/mol%	52	65	72
P_{ob} [a]	0.52	0.65	1
ξ^2 [b]	0.52	0.81	1

[a] $\bar{P}_{ob}=(1/3)\sum_{\gamma} P_{ob}(\gamma)$, $\gamma=0$, 45 and 90°.

[b] $\xi=x/72$, in which x is the VDF molar content.

Table VI. Comparison between the theoretical and the experimental values of T_1's in the VDF/TrFE copolymers for $\gamma=0$, 45, and 90° at 110 and 120°C in the cooling process. The values of T_1 which are shown in the parentheses are calculated from the experimental value in P(VDF_{72}/$TrFE_{28}$) by using the scaling factor ξ (see eq 6)

		72/28	65/35	52/48
T		T_1	T_1	T_1
°C	(°)	ms	ms	ms
	0	91.8	134.2 (113.0)	178.0 (176.5)
110	45	120.9	169.4 (149.3)	225.0 (231.0)
	90	127.0	194.7 (156.8)	248.0 (244.2)
	0	101.0	164.7 (124.7)	194.8 (194.2)
120	45	129.8	209.3 (160.2)	251.2 (249.6)
	90	147.0	223.4 (185.1)	288.5 (282.7)

$$\xi=x/72 \qquad \text{(5b)}$$

The P_{ob} (γ)'s calculated from the experimental data of the copolymers do not almost depend on the angle γ in the temperature region between 100 and 120°C (↓). The values of the averaged $\bar{P}_{ob}$, $\bar{P}_{ob}=1/3\sum_{\gamma} P_{ob}$ (γ) ($\gamma=0$, 45, and 90°), and ξ^2 against the VDF content of 'x' are listed in Table V. The values of $\bar{P}_{ob}$ coincide approximately with those of ξ^2. Therefore, using the parameter ξ^2 in the stead of the $\bar{P}_{ob}$, the $(1/T_1)_{72}$ is written by

$$\left(\frac{1}{T_1}\right)_{72}(\gamma)=\xi^{-2}\left(\frac{1}{T_1}\right)_{ob}(\gamma) \qquad (6)$$

Therefore, using eq 1 and 6, the correlation time τ_D for each copolymer transforms according to

$$\tau_{D72}=\xi^{-4}\tau_D \qquad (7)$$

where τ_{D72} is the correlation time for P(VDF_{72}/$TrFE_{28}$). Therefore, the VDF content is strongly related to the T_1 and τ_D. The values of T_1 at 110°C (↓) and 120°C (↓) for P(VDF_{52}/$TrFE_{48}$) and P(VDF_{65}/$TrFE_{35}$) which are calculated from that in P(VDF_{72}/$TrFE_{28}$) by using the scaling factor are shown in the parentheses in Table VI and are compared with the values of $(T_1)_{ob}$ for P(VDF_x/$TrFE_{100-x}$) ($x=52$ and 65 mol%) observed at 110 and 120°C in the cooling process. The agreements between the calculated values and experimental data are qualitatively good although the calculated values for P(VDF_{65}/$TrFE_{35}$) are smaller than the experimental data.

CONCLUSION

For the drawn films of P(VDF_{52}/$TrFE_{48}$) and P(VDF_{65}/$TrFE_{35}$), three kinds of the spin lattice relaxations were observed below the Curie temperature T_c, around T_c and in a higher temperature region above T_c, respectively, which are referred to as β, α_t, and α_b'. They were compared with those of P(VDF_{72}/$TrFE_{28}$) reported in Part I of this series.[3] The values of T_1 for the β relaxation became larger in order of the VDF content $x=72$, 52, and 65 mol%, which may be attributed to the motion of the chain backbone in partially crystalline regions. The T_1 for α_t relaxation in each copolymer was minimal at T_c due to the phase transition. The T_1 *vs.* T curve showed more largely thermal hysteresis with increasing of VDF content, of which the temperature of the T_1 minimum agreed approximately with the Curie temperature. The value of T_1 in the phase transition region became smaller in order of 65, 52, and 72 mol%.

The T_1's for the α_b' relaxations in P(VDF_{52}/$TrFE_{48}$) and P(VDF_{65}/$TrFE_{35}$) were analyzed, respectively, on the basis of Bloembergen's thoery,[4] in terms of the non-exponential correlation function obtained by Hunt and Powles.[5] The existence of the one-dimensional diffusion motion of the conformational defect in each copolymer was verified from the reasonable agreements between the theoretical and experimental results. The activation energy of the 1-D diffusion motion did not depend on the VDF content, which was about 8.5 kcal mol^{-1}. The $(1/T_1)$'s and the correlation times of the local field modulated by the 1-D diffusion motion in P(VDF_{52}/$TrFE_{48}$) and P(VDF_{65}/$TrFE_{35}$) were converted approximately to those in P(VDF_{72}/$TrFE_{28}$) with the scaling factors of ξ^{-2} and ξ^{-4}, respectively, in which ξ is the ratios of the VDF content of 52 and 65 mol% to 72 mol%. This means that the VDF content has a great influence on the 1-D diffusion motion.

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