Ferroelectric Transition in Vinylidene Fluoride and Trifluoroethylene Copolymers Studied by NMR Method

II. 52 and 65 mol% Vinylidene Fluoride Copolymers

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(Received May 21, 1990)

ABSTRACT: NMR derivative line shapes $f'(\Delta H)$ in vinylidene fluoride (VDF)/trifluoroethylene (TrFE) copolymers with VDF contents of 52 and 65 mol% were measured as a function of the alignment angle γ between the drawn axis and magnetic field over a temperature range between 20 and 130°C. The fine structure of $f'(\Delta H)$ and the motional narrowings of the line widths in the each copolymer were investigated by comparing them with those for VDF 72 mol% copolymer. In the ferroelectric phase, $f'(\Delta H)$'s in VDF 65 and 72 mol% copolymers consisted of three components of narrow, intermediate and broad line widths (ΔH_s , ΔH_m , and ΔH_b), ΔH_m and ΔH_b which were due to the TrFE and VDF groups, respectively; $f'(\Delta H)$ in the VDF 52 mol% copolymer had two components of ΔH_s and ΔH_b . The value of ΔH_b was almost equal to ΔH_m in 65 and 72 mol% copolymers. When VDF content decreased, the flip-flop motion of TrFE groups in the VDF 72 mol% copolymer changed into rotational motion around the chain axis. Near the Curie temperature, T_c two kinds of trans VDF group motion around the chain axis and TrFE group motion coordinate with the VDF rotational motion disappeared in the VDF 52 mol% copolymer. At the T_c , ΔH_b discontinuity for each copolymer was observed, but the thermal hysteresis of ΔH_b vs. temperature decreased as VDF content decreased, and was not significant in the VDF 52 mol% copolymer. These findings suggest that the ferroelectric phase transition is of the first order above VDF 65 mol%, and of the first order close to the second order for VDF 52 mol%.

KEY WORDS NMR Line Widths / Narrowing Processes / Vinylidene Fluoride and Trifluoroethylene Groups / Vinylidene Fluoride content / Motional Modes / Ferroelectric Phase Transition /

Vinylidene fluoride (VDF) and trifluoroethylene (TrFE) copolymer is a ferroelectric of order-disorder type, which exhibits structure phase transition, accompanied by conformational changes between the trans chain in the ferroelectric phase and statistical mixture chain of TGT $\bar{G}$ and T₃GT₃ $\bar{G}$ conformers in the paraelectric phase. The phase transition changes from second order to first order with increasing VDF contents of 52 to 80 mol%, and thermal hysteresis of the phase transition appears more clearly above VDF 65 mol%. Odajima¹ and Tashiro *et al.*² have shown that,

when the energy difference of the trans to the gauche form, $\Delta U (=U_{tt} - U_{tg}) > 0$, is positive, this transition is first order and its thermal hysteresis becomes larger.

Anomalous increases of the dielectric constant for the copolymers with VDF contents of 52, 65, and 72 mol% have been observed in the vicinity of the Curie temperature T_c in rising and falling temperature processes (hereafter, referred to as arrow signs $\uparrow$ and $\downarrow$, respectively).^{3,4,5} If the critical fluctuation of polarization takes place near T_c , anomalous increase of the dielectric relaxation strength $\Delta\epsilon$

and critical slowing down of the relaxation time τ are expected to be maximal for the VDF 52 mol% copolymer since the phase transition is second-order. However, anomalies of $\Delta\epsilon$ and τ in the copolymers increased progressively with VDF 72, 52, and 65 mol%. Ohuchi *et al.*⁶⁾ suggest that the motion of the electrical chain dipoles, with a relaxation time τ_0 , may be associated with the thermal conformation fluctuation of certain segments at boundary regions between the trans and statistical mixture segments near T_c . The number of segments becomes larger in the following order: 65 > 52 > 72 mol%. However, further reports have not been specially focused on the dependence of VDF content in $\Delta\epsilon$ and τ .

In a previous paper,⁷ we investigated the ferroelectric phase transition mechanism for the drawn film of the VDF/TrFE copolymer with a VDF content of 72 mol%, on the basis of the motional characteristics of the chain in the ferroelectric and paraelectric phases, by using NMR method. In the ferroelectric phase, the observed NMR derivative line shape $f'(\Delta H)$ consisted of three components of narrow, intermediate and broad line widths (ΔH_s , ΔH_m , and ΔH_b). ΔH_m and ΔH_b were attributed to the TrFE and VDF groups in the trans chain in the ferroelectric crystalline region, respectively. ΔH_s was due to the amorphous region, whose fraction was 0.05. In the paraelectric phase, $f'(\Delta H)$ consisted of two components of narrow and broad line width (ΔH_s and ΔH_b), of which ΔH_b was attributed to the statistical mixture chain of TGT $\bar{G}$ and T₃GT₃ $\bar{G}$ conformers in the crystalline region². ΔH_m , ΔH_b , and ΔH_s depended on the alignment angle γ between the drawn direction and magnetic field.

The motional narrowing of the NMR second moment $\langle\Delta H^2\rangle$ was observed in the four temperature regions of the $\uparrow$ -process. The motion narrowing processes in the respective regions were referred to as α_m , α_b (β_m), α_t , and α_b . The broadening of $\langle\Delta H^2\rangle$ took place in the three temperature regions of the $\downarrow$ -process;

the broadening processes in respective region were referred to as α_b , α_t , and α_m . The variation of the second moment, $\delta\langle\Delta H^2\rangle$, taking place in each temperature region, showed strong γ -dependence. In the $\alpha_t\uparrow$ and $\alpha_t\downarrow$ regions, narrowing temperatures of $\langle\Delta H^2\rangle$ equaled the Curie temperatures of $T_{c\uparrow}$ and $T_{c\downarrow}$, respectively, which were obtained from DSC and dielectric measurements. The $\delta\langle\Delta H^2\rangle$ against γ in the respective α_t regions displayed a concave curve. This may be attributed to a motion mode of the VDF segments accompanying the conformational change between the all-trans form and the gauche form. In the ferroelectric phase, $\delta\langle\Delta H^2\rangle$ against angle γ in the α_m region displayed a convex curve, which was explained theoretically as a flip-flop motion of a trans TrFE group between two sites 180° apart, accompanied by rotational oscillation 40° in amplitude. In the α_b (β_m) region, $\delta\langle\Delta H^2\rangle$ vs. γ curve increased with increasing angle γ for the broad-line component, but the curve for the whole line shape was concave. The γ -dependence of the broad component curve was due to the motional mode in which VDF groups in the trans chain oscillated about the chain axis with an amplitude of 10°. The concaveness of $\delta\langle\Delta H^2\rangle$ vs. γ curve for the whole shape was associated with motion broadening of ΔH_m (referred to as β_m) in the α_b (β_m) region, attributed to motion of the TrFE group, coordinated with rotational motion of the VDF group.

At a higher temperature in the paraelectric phase, the γ -dependence of NMR line width ΔH_b was interpreted as one-dimensional diffusion motion of conformational defects along the chain axis. Near T_c in the α_b region, slight increase of ΔH_b was theoretically analyzed in the random phase approximation of the Ising model.⁸ It was shown that the increase of ΔH_b is due to cooperative fluctuation of polarization between trans segments having the electric dipole moment and diffuse phase transition of a first order near T_c .⁸

In this paper, NMR derivative absorption curves $f'(\Delta H)$ for the drawn films of the VDF 52 and 65 mol% copolymers were measured as functions of T and γ , and fine structures and motional modes of the chain in the ferroelectric and paraelectric phases are studied by comparing them by those for the VDF 72 mol% copolymer. Also discussed is how their dependence on VDF content is associated with the behavior of the ferroelectric phase transition when VDF content decreases from 72 to 52 mol%.

EXPERIMENTAL

Samples used were random copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) with VDF contents of 52, and 65 mol% supplied by Daikin Kogyo Co., Ltd. Hereafter, the copolymer with x mol% VDF content is referred to as either P(VDF _{x} /TrFE_{100- x}) or the VDF x mol% copolymer. Copolymer films were prepared by slowly casting from 2-butanone solutions under atmospheric pressure at room temperature, and were then drawn $\times 6$ uniaxially. The drawn films of P(VDF₅₂/TrFE₄₈) and P(VDF₆₅/TrFE₃₅) were annealed at 130°C for 20 hr and 9 hr while pressed between glass plates. The final draw ratios for P(VDF₆₅/TrFE₃₅) and P(VDF₅₂/TrFE₄₈) were 4 and 4.5, respectively. Procedures were carried out under the same conditions as those used in preparing samples for T_1 measurements.^{9,10}

The NMR line shapes in both the copolymers were measured for $\gamma = 0, 45, \text{ and } 90^\circ$ by a wide line NMR spectrometer, operating at 40 MHz over a temperature range between 20 and 130°C.

RESULTS

NMR Derivative Line Shapes

Figure 1a and b show the right halves of the NMR derivative curves $f'(\Delta H)$ for P(VDF₅₂/TrFE₄₈), P(VDF₆₅/TrFE₃₅), and P(VDF₇₂/

TrFE₂₈) at 30 and 125°C in the $\uparrow$ -process for $\gamma = 0, 45, \text{ and } 90^\circ$. P(VDF₇₂/TrFE₂₈) curves have been reported in the previous paper.⁷ For $\gamma = 0$ and 90° and 30°C, $f'(\Delta H)$ for P(VDF₅₂/TrFE₄₈) consists of two peaks, which correspond to broad and narrow widths (ΔH_b and ΔH_s). On the other hand, the $f'(\Delta H)$'s for P(VDF₆₅/TrFE₃₅) and P(VDF₇₂/TrFE₂₈) consist of three peaks, which correspond to broad, intermediate and narrow widths (ΔH_b , ΔH_m , and ΔH_s). However, $f'(\Delta H)$ for $\gamma = 45^\circ$ in P(VDF₆₅/TrFE₃₅) shows two peaks of narrow and broad widths. The broad width component seems to be made up of ΔH_b and ΔH_m , although they are not separated. In Figure 1b, all $f'(\Delta H)$'s show two peaks of narrow and broad widths (ΔH_s and ΔH_b), at 125°C for $\gamma = 0, 45, \text{ and } 90^\circ$. ΔH_b and ΔH_s for all copolymers, and ΔH_m for VDF 65 and 72 mol% copolymers, depend on angle γ , while those for ΔH_s and ΔH_s do not. The narrow component fraction in $f'(\Delta H)$, observed over the temperature range between 30 and 130°C, was approximately 4% for VDF 52 mol% copolymer and 6% for the VDF 65 mol% copolymer. The fractions were evaluated by the Willson and Pake' method.¹¹

Line Width and Its Temperature Dependence

Figure 2a and b show the line widths in P(VDF₆₅/TrFE₃₅), plotted against temperature, for $\gamma = 0$ and $45, \text{ and } 90^\circ$. In the temperature region between 50 and 85°C for the $\uparrow$ - and $\downarrow$ -processes, the ΔH_b component appeared as the shoulder of the intermediate component in the respective line shapes for $\gamma = 0$ and 90° . Therefore, line width value were plotted as $\bullet$ and $\circ$ for the $\uparrow$ - and $\downarrow$ -processes, respectively; These corresponded to maximum point of the shoulder.

In the $\uparrow$ -process, ΔH_b s for $\gamma = 0$ and 90° narrow abruptly in temperature regions between 80 and 90°C and between 70 and 80°C, respectively, and then narrow slightly up to 125°C. The respective narrowing processes of ΔH_b for each angle are referred to as $\alpha_a(\uparrow)$ and $\alpha_b(\uparrow)$, respectively, in the order of increasing

Figure 1. Derivative NMR absorption line shapes of VDF/TrFE copolymers with VDF content of 52, 65, and 72 mol% for 0, 45, and 90° of the alignment angle between the drawn axis and the magnetic field; (a) 30°C and (b) 125°C.

temperature. On the other hand, ΔH_b s for $\gamma=45^\circ$ decrease between 40 and 70°C and between 75 and 85°C.

ΔH_m s for $\gamma=0$ and 90° gradually decrease by about 3 Gs between 40 and 70°C and by 2 Gs between 35 and 65°C, respectively, and then increase gradually by 1–2 Gs up to 105°C. ΔH_m seems to approach ΔH_b above 100°C, except for $\gamma=45^\circ$. The narrowing and broadening processes of ΔH_m for each angle γ are referred to as $\alpha_m(\uparrow)$ and $\beta_m(\uparrow)$, respectively, in the order of increasing temperature. The temperature regions of α_x ($x = m, b, t$, etc.) and β_m are referred to as α_x and β_m regions, respectively. Since $\alpha_b(\uparrow)$ and $\beta_m(\uparrow)$ processes take place in the same temperature region, their temperature region is referred to as $\beta_m(\alpha_b)$.

Broadening of 0.5–1.2 Gs was observed for ΔH_b between 125 and 80°C in the $\downarrow$ -process, which is referred to as $\alpha_b(\downarrow)$. The line width (○) extremely broadens between 78 and 74°C

and then returns to the value of ΔH_b in the $\uparrow$ -process. The intermediate width simultaneously appears at 69°C, and decreases between 69 and 50°C; it then returns to the value of ΔH_m in the α_m region of the $\uparrow$ -process. Extreme broadening of ΔH_b , and narrowing of ΔH_m in the $\downarrow$ -process are referred to as $\alpha_t(\downarrow)$ and $\beta_m(\downarrow)$, respectively. The line width of ΔH_b for $\gamma=45^\circ$ broadens gradually in the $\alpha_b(\downarrow)$ region and increases abruptly in the $\alpha_t(\downarrow)$ region, and then returns to the value of the $\uparrow$ -process.

Figure 3 shows the line width in P(VDF₅₂/TrFE₄₈), plotted against temperature, for $\gamma=0$, 45, and 90° . In the $\uparrow$ -process, line widths ΔH_b s for $\gamma=0$, 45, and 90° narrow gradually between 40 and 60°C, decrease abruptly between 60 and 70°C, and then decrease slightly between 70 and 125°C. The narrowing processes of ΔH_b in the $\uparrow$ -process are referred to as α_m , α_t , and α_b , respectively, in the order of increasing temperature. The temperature region of the α_x

Figure 2. Line widths of P(VDF₆₅/TrFE₃₅) as a function of temperature: (a) $\gamma = 0^\circ$ and 45° ; (b) $\gamma = 90^\circ$. The filled and unfilled marks of circle and triangle indicate the broad widths in the $\uparrow$ - and $\downarrow$ -processes, respectively and those of square indicate the intermediate widths in the $\uparrow$ - and $\downarrow$ -processes, respectively.

($x = m, t, b'$) is referred to as α_x region. It should be noted that ΔH_b s for $\gamma = 0^\circ$ discontinuously decrease in the α_t region, although decrement of ΔH_b is smaller than those of the other angles. In the $\downarrow$ -process, ΔH_b s increase in the same three temperature regions as $\alpha_{b'}$, α_t , and α_m in the $\uparrow$ -process; These ΔH_b s show reversible changes under $\uparrow$ - and $\downarrow$ -conditions.

The $\alpha_m\uparrow$, $\beta_m(\alpha_b)\uparrow$, $\alpha_t\uparrow$, $\alpha_b'\uparrow$, $\alpha_b'\downarrow$, $\alpha_t\downarrow$, $\beta_m\downarrow$, and $\alpha_m\downarrow$ regions for P(VDF₆₅/TrFE₃₅), and the α_m , α_t and $\alpha_{b'}$ regions in the $\uparrow$ - and $\downarrow$ -processes for P(VDF₅₂/TrFE₄₈) are respectively sum-

Figure 3. Line widths of P(VDF₅₂/TrFE₄₈) as a function of temperature in the $\uparrow$ - and $\downarrow$ -processes. Line width values for $\gamma = 0^\circ$ are indicated by filled circle in the $\uparrow$ -process and unfilled circle in the $\downarrow$ -process ($\bullet$, $\circ$); those for $\gamma = 45^\circ$ are indicated by triangles ($\blacktriangle$, $\triangle$); those for $\gamma = 90^\circ$ are indicated by square ($\blacksquare$, $\square$).

Table I. Classification of motion states and transition temperatures for P(VDF₆₅/TrFE₃₅)

$\uparrow$ -process		$\downarrow$ -process	
Motion state	Temperature region °C	Motion state	Temperature region °C
$\alpha_m\uparrow$	40—70	$\alpha_m\downarrow$	50—40
$\beta_m(\alpha_b)\uparrow$	70—80	$\beta_m\downarrow$	69—50
$\alpha_t\uparrow$	80—90	$\alpha_t\downarrow$	78—74
$\alpha_{b'}\uparrow$	90—110	$\alpha_{b'}\downarrow$	110—78

Table II. Classification of motion states and transition temperatures for P(VDF₅₂/TrFE₄₈)

$\uparrow$ -process		$\downarrow$ -process	
Motion state	Temperature region °C	Motion state	Temperature region °C
$\alpha_m\uparrow$	40—60	$\alpha_m\downarrow$	60—40
$\alpha_t\uparrow$	60—70	$\alpha_t\downarrow$	70—60
$\alpha_{b'}\uparrow$	70—110	$\alpha_{b'}\downarrow$	110—70

Figure 4. Temperature changes of the NMR second moments, $\langle \Delta H^2 \rangle(\gamma)$'s for P(VDF₆₅/TrFE₃₅): (a) values of $\langle \Delta H^2 \rangle$ in the $\uparrow$ - and $\downarrow$ -processes are indicated, respectively, by the filled and unfilled marks of $\bullet, \circ$ for $\gamma=0^\circ$, and those of $\blacktriangle, \triangle$ for $\gamma=45^\circ$; (b) filled and unfilled squares of $\blacksquare, \square$ are the values of $\langle \Delta H^2 \rangle$ for $\gamma=90^\circ$ in the $\uparrow$ - and $\downarrow$ -processes, respectively.

marized in Tables I and II.

NMR Second Moment and Mobile Fraction

Figure 4a and b show temperature changes of the NMR second moments, $\langle \Delta H^2 \rangle(\gamma)$ s in P(VDF₆₅/TrFE₃₅) for $\gamma=0, 45$, and 90° . The $\langle \Delta H^2 \rangle$ s for $\gamma=0^\circ$ in the $\uparrow$ - and $\downarrow$ -processes respectively are indicated by filled and unfilled circles ($\bullet, \circ$); those of for $\gamma=45^\circ$ are indicated by triangles ($\blacktriangle, \triangle$) and those for $\gamma=90^\circ$ by

Figure 5. Temperature changes of the NMR second moment, $\langle \Delta H^2 \rangle(\gamma)$'s for P(VDF₅₂/TrFE₄₈): (a) Values of $\langle \Delta H^2 \rangle$ in the $\uparrow$ - and $\downarrow$ -processes are indicated respectively by the filled and unfilled marks of $\bullet, \circ$ for $\gamma=0^\circ$, and those of $\blacktriangle, \triangle$ for $\gamma=45^\circ$; (b) filled and unfilled squares of $\blacksquare, \square$ are the values of $\langle \Delta H^2 \rangle$ for $\gamma=90^\circ$ in the $\uparrow$ - and $\downarrow$ -processes, respectively.

squares ($\blacksquare, \square$). In the $\uparrow$ -process, $\langle \Delta H^2 \rangle$ for $\gamma=0, 45$, and 90° decreases gradually in the α_m region and extremely in the wide temperature range over the $\beta_m(\alpha_b)$, α_i , and α_b regions. The latter narrowing process is referred to as $\alpha'_i(\uparrow)$. The $\alpha'_i(\uparrow)$ s for $\gamma=45$ and 90° take place in a $5\text{--}10^\circ\text{C}$ lower temperature region than the α'_i region for $\gamma=0^\circ$. When temperature falls, $\langle \Delta H^2 \rangle$ for each angle γ increases slightly 1–3 Gs in the α_b region. Furthermore, the values of $\langle \Delta H^2 \rangle$ increase abruptly in $\alpha'_i(\downarrow)$ region and

return to $\langle\Delta H^2\rangle$ in the α_m region of the $\uparrow$ -process. Decrements of $\langle\Delta H^2\rangle$, $\delta\langle\Delta H^2\rangle$ in the α_m and α_t regions depend on the angle γ . The fraction, F_m of the narrow and intermediate components increased by 12 and 40% in the α_m and $\beta_m(\alpha_b)$ regions, respectively.

Figure 5a and b show the temperature changes of the NMR second moment, $\langle\Delta H^2\rangle(\gamma)$ for P(VDF₅₂/TrFE₄₈). $\langle\Delta H^2\rangle$ s in the $\uparrow$ - and $\downarrow$ -processes respectively are indicated by filled and unfilled circles (●, ○); those of for $\gamma=45^\circ$ are indicated by triangles (▲, △) and those for $\gamma=90^\circ$ by squares (■, □). The $\langle\Delta H^2\rangle$ vs. T curve for each γ decreases in three stages over the wide temperature range of the α_m , α_t and α_b' regions. Thermal hysteresis does not take place in these $\uparrow$ - and $\downarrow$ -processes. $\delta\langle\Delta H^2\rangle$ in each temperature region increases with increasing angle γ . The F_m of the narrow component decreases 3 to 4% in the α_t region.

DISCUSSION

Line width estimation of $f'(\Delta H)$ depends on VDF content

In Figure 1, comparing ΔH_m and ΔH_b of $f'(\Delta H)$ in P(VDF₆₅/TrFE₃₅) for each γ with those of P(VDF₇₂/TrFE₂₈), ΔH_b and its component fractions in $f'(\Delta H)$ decrease; ΔH_m however does not change significantly, though its component fraction increases. For P(VDF₅₂/TrFE₄₈), ΔH_b is similar to the value of ΔH_m for the TrFE group in P(VDF₇₂/TrFE₂₈).⁷ These findings suggest that ΔH_m for the VDF 65 mol% copolymer and ΔH_b for the VDF 52 mol% copolymer may be attributed to the TrFE groups of the trans chain in the ferroelectric phase. At 125°C, the value of ΔH_b in $f'(\Delta H)$ at each angle γ has the same value for all copolymers, which may be attributed to fluctuation of the local magnetic field which is modulated by the one-dimensional diffusion motion of the conformational defects in the paraelectric phase.

Molecular Motions in Ferroelectric and Paraelectric Phases

The thermal hystereses of $\Delta H_b(\gamma)$ and $\langle\Delta H^2\rangle(\gamma)$ in P(VDF_{*x*}/TrFE_{100-*x*}) become smaller in the order of decreasing VDF content x , from 72 to 52 mol%, as shown in Figures 2–5. The abrupt change of the broad line width between ΔH_b and $\Delta H_{b'}$ in each copolymer for $\gamma=0^\circ$ takes place in the $\alpha_t\uparrow$ and $\alpha_t\downarrow$ regions as shown in Figures 2 and 3, whereas the change in $f'(\Delta H)$, as shown in Figure 1a and b, took place discontinuously. The narrowing temperatures of ΔH_b which changed discontinuously in the α_t region are listed in Table III as $T_c(\uparrow)$ and $T_c(\downarrow)$ for the $\uparrow$ - and $\downarrow$ -processes. Narrowing temperatures for P(VDF₇₂/TrFE₂₈) were reported in a previous paper.⁷ Both $T_c(\uparrow)$ and $T_c(\downarrow)$ shift to lower temperatures when VDF content decreases. They approximate the corresponding transition temperatures obtained from dielectric,⁴ DSC,⁴ and spin lattice relaxation time measurements.^{9,10} The narrowings of ΔH_b in the α_t region for the VDF 52 and 65 mol% copolymers may also be due to ferroelectric phase transition. The discontinuous variation of ΔH_b in each α_t region and its thermal hysteresis decrease in the order of VDF 75 and 65 mol%. In the 52 mol% copolymer the latter is not significant, but the former occurs slightly at $T_c=63^\circ\text{C}$. Such dependences of VDF content in the discontinuous change of ΔH_b and its thermal hysteresis show that

Table III. Temperatures of α_t processes for three VDF/TrFE copolymers with the VDF contents of 52, 65 and 72 mol% in 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	
ΔH	63	63	89	70	116	75
T_1	65	65	90	75	115	79
DSC	60	62	70	64	114	75
$1/\Delta\epsilon$	79	73	102	69	134	84

this phase transition is of the first order for VDF 65 and 72 mol%, and that, especially, it is first order close to the second order for VDF 52 mol%.

ΔH_b for the VDF 52 mol% copolymer and ΔH_m for the VDF 65 mol% copolymers narrow extremely at about 50°C in the α_m regions, as does the ΔH_m of P(VDF₇₂/TrFE₂₈).⁷ This means that the narrowing temperature of α_m , due to the motion of the TrFE group, does not depend on VDF content, although the temperature range of α_m decreases with decreasing VDF content as shown in Tables I and II.

In a previous paper,⁷ narrowing of ΔH_b s and broadening of ΔH_m in P(VDF₇₂/TrFE₂₈) in the $\uparrow$ -process took place simultaneously between 80 and 110°C in the $\alpha_b(\beta_m)$ region below $T_c(\uparrow)$. These were attributed respectively to the rotational motion of the VDF groups in the trans chain with amplitude of 10° around the axis and TrFE group motion coordinated with the rotational motion of the VDF group.

As shown in Figure 2, ΔH_m in P(VDF₆₅/TrFE₃₅) broadens slightly in the $\beta_m(\alpha_b)$ region near T_c , as it also does in the $\alpha_b(\beta_m)$ region for P(VDF₇₂/TrFE₂₈).⁷ The narrowing stages of ΔH_b and $\langle\Delta H^2\rangle$ in P(VDF₆₅/TrFE₃₅) are not observed clearly in the $\beta_m(\alpha_b)$ region below $T_c(\uparrow)$, as shown in Figures 2 and 4, since the ferroelectric phase transition takes place at $T_c(\uparrow)=90^\circ\text{C}$. However, for $\gamma=45$ and 90° , extreme decrease in ΔH_b and $\langle\Delta H^2\rangle$ takes place, respectively, in a 5 to 10°C lower temperature region than the α_t narrowing region for $\gamma=0^\circ$, where ΔH_b vs. T curve for $\gamma=0^\circ$ hardly changes. These findings suggest that in P(VDF₆₅/TrFE₃₅) two kinds of α_b motion mechanisms may exist: the rotational motion of the VDF groups around the chain axis and increase of ΔH_m may be attributed to the TrFE group motion coordinated with the rotational motion of VDF groups in the $\beta_m(\alpha_b)$ region below $T_c(\uparrow)$, as they also do in P(VDF₇₂/TrFE₂₈). On the other hand, although ΔH_b in the VDF 52 mol% copolymer is due to the TrFE groups, broadening of ΔH_b ,

which corresponds to β_m in other copolymers, is never observed near $T_c(\uparrow)$. The disappearance of α_b and β_m may be closely associated with the stability of a trans VDF segment^{1,2} near $T_c(\uparrow)$; This suggests that TrFE group motion, coordinated with the rotational motion of the VDF groups, may play an essential role in stabilizing the trans VDF segment.^{2,7}

In the paraelectric phase, as shown in Figures 2–4, when VDF content decreases, the slight increases of ΔH_b and $\langle\Delta H^2\rangle$ in the α_b region occur at lower temperatures in company with depression of $T_c(\uparrow)$. They increase in increments, becoming larger with decreasing VDF content. In previous papers,^{6,7} the respective increments of ΔH_b and inverse spin-lattice relaxation time $1/T_1$ in the α_b region for each copolymer, were analyzed theoretically on the basis of the Ising model. It was shown that phase transition diffuseness takes place in the critical region close to $T_c(\uparrow)$, that phase transition region becomes larger with decreasing VDF content, and that polarization fluctuation near T_c increases progressively with VDF 72, 52, and 65 mol%. The shift of α_b to low temperature and temperature increase of the diffuse phase transition region may be attributed to the stability of the VDF trans segment. The energy difference of trans and gauche causes changes from positive to

Figure 6. Decrement of the second moment, $\delta\langle\Delta H^2\rangle$ within the following regions of P(VDF₅₂/TrFE₄₈) as a function of alignment angle γ between the drawn direction of the film and the magnetic field: (a) and (b) are the $\delta\langle\Delta H^2\rangle$ vs. γ curves in the α_m and α_t regions, respectively.

Figure 7. Decrement of the second moment, $\delta\langle\Delta H^2\rangle$ within the following regions of P(VDF₆₅/TrFE₃₅) as a function of alignment angle γ between the drawn direction of the film and the magnetic field; (a) α_m : $\circ$, $\delta\langle\Delta H^2\rangle$, (b) $\alpha_t^\uparrow$: $\circ$, $\delta\langle\Delta H^2\rangle$ and (c) $\alpha_t^\downarrow$: $\circ$, $\delta\langle\Delta H^2\rangle$, respectively.

negative with decreasing VDF content.^{1,2}

Figures 6 and 7 show the dependencies of $\delta\langle\Delta H^2\rangle$ on angle γ in the α_m and α_t regions for P(VDF₅₂/TrFE₄₈), and in the α_m and α_t' regions for P(VDF₆₅/TrFE₃₅).

$\delta\langle\Delta H^2\rangle$ vs. γ curves in the $\alpha_t^\uparrow$ and $\alpha_t^\downarrow$ regions are concave for P(VDF₆₅/TrFE₃₅) in Figure 7. They are also concave for P(VDF₇₂/TrFE₂₈),⁷ but for P(VDF₅₂/TrFE₄₈) they increase with increasing γ . The concaveness of the $\delta\langle\Delta H^2\rangle$ against γ is characteristic of the ferroelectric phase transition of the first order accompanied by conformational change of the VDF segment from trans to gauche. The change of $\delta\langle\Delta H^2\rangle$ vs. γ curve in the α_t region, coupled with decrease of VDF content from 65 to 52 mol%, is associated closely with the appearance of the ferroelectric phase transition which changed from first-order to second-orderlike. This may be attributed to the more stable trans conformation of the VDF segment rather than to the gauche one.^{1,2}

$\delta\langle\Delta H^2\rangle$ plotted against the γ in the α_m region for the 52 and 65 mol% copolymers increased with increasing γ , in contrast to the convex curve which was maximal at $\gamma=45^\circ$ for the

72 mol% copolymer. This change of the $\delta\langle\Delta H^2\rangle$ vs. γ curve in the α_m region suggests that the motional mode of the TrFE group changed, under the influence of decreasing VDF content, from flip-flop motion⁷ to rotational motion around the chain axis. This further suggests that the ferroelectric feature of the phase transition depends on VDF content and greatly influences the motion modes of the VDF and TrFE groups in the chain in the ferroelectric phase as well as the disappearances of α_b and β_m below $T_c(\uparrow)$ in the VDF 52 mol% copolymer.

CONCLUSIONS

The fine structure, the motion modes of the chain, and ferroelectric phase transition in the copolymers were investigated by comparing NMR line shapes $f'(\Delta H)$ and the motional narrowings of the line width ΔH and the second moment $\langle\Delta H^2\rangle$ in ferroelectric and paraelectric phases for 52 and 65 mol% copolymers with those in the VDF 72 mol% copolymer.⁷

Below T_c , $f'(\Delta H)$ consisted of three components of narrow, intermediate and broad line widths (ΔH_s , ΔH_m , and ΔH_b) for the VDF 65 mol% copolymer and two components of, ΔH_s and ΔH_b , for the VDF 52 mol% copolymer. ΔH_s was due to the amorphous chain. ΔH_b and ΔH_m in the ferroelectric phase for the VDF 65 mol% copolymer, were attributed to VDF and TrFE groups in the trans chains, respectively, as were those for the VDF 72 mol% copolymer. The value of ΔH_b in P(VDF₅₂/TrFE₄₈) was equal to the value of ΔH_m for other copolymers, which was attributed to TrFE groups in the trans chain. Above T_c , $f'(\Delta H)$'s for all copolymers consisted of two components of narrow and broad line widths (ΔH_s and ΔH_b), respectively. $f'(\Delta H)$ in the paraelectric phase did not show the fine structure of the VDF and TrFE groups; ΔH_b was due to the whole statistical chain of TGTG and T₃GT₃G.

The ferroelectric feature of the phase

transition depended on VDF content and greatly influenced the motion modes of VDF and TrFE groups of the chain in the ferroelectric phase as follows:

(1) The α_m process was attributed to the motion of TrFE groups in the ferroelectric phase; the motion mode of TrFE groups changed from flip-flop motion to a rotational oscillation, when the VDF content decreased from 72, through 65 and 52 mol%.

(2) The $\beta_m(\alpha_b)$ process was attributed to the rotational motion of VDF groups around the trans chain axis (α_b) and motion of TrFE groups, coordinating with the VDF rotational motion (β_m) in the $\beta_m(\alpha_b)$ region near T_c in conditions of rising temperature. These motions occurred in the VDF 72 and 65 mol% copolymers, but did not in the 52 mol% copolymer.

(3) The α_t process was due to the ferroelectric phase transition accompanied by the conformational change of the VDF segment. The discontinuity of ΔH_b at T_c and its thermal hysteresis of α_t confirmed that the ferroelectric phase transition is first order for VDF 65 and 72 mol% copolymers and first order close to second order for the VDF 52 mol% copolymer.

The α_b process in the paraelectric phase

was attributed to the polarization fluctuation of trans segments (order units) near $T_c(\downarrow)$.

Acknowledgments. The authors are grateful to Drs. Jun Koizumi, Junichi Sako, Toshiharu Yagi and Yoshihide Higashihata of Daikin Kyogyo Co., Ltd., for supplying the samples of VDF/TrFE copolymers.

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