

STUDIES ON THE CHAIN STRUCTURAL EFFECT OF PVDF AND VDF(52)/TrFE(48) COPOLYMER BY MEANS OF THE METHOD OF DIELECTRIC RELAXATION*

ZHANG Xingyuan(张兴元)

(*Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026*)

FURUKAWA, Takeo

(*Department of Chemistry, Science University of Tokyo, Japan*)

ABSTRACT

Through improvements on a fully commercial and automatic system measuring frequency and temperature spectra of the complex elastic, dielectric, and piezoelectric constants of polymer films, the precision for measuring complex dielectric constants achieved 2% from original 1%. The complex dielectric constants of PVDF, VDF(95)/VF(5), VDF(52)/TrFE(48) and VDF(47.5)/TrFE(47.5)/HeFP(5) over a range of $-120-140^{\circ}\text{C}$, $10^{-2}-10^4\text{Hz}$ were measured by the described system. The diminution of chain regularity due to 5mol% vinyl fluoride in the chain of PVDF led to disappearing of α -relaxation and increase in T_g (3°C) of VDF(95)/VF(5). Because of the spatial impediment of 5mol% HeFP in copolymer chain, the Curie point of VDF(52)/TrFE(48) decreased by 30°C and T_g by 3°C . The behavior of dielectric relaxation indicated that 5mol% vinyl fluoride and HeFP made the relaxation strength of noncrystalline region reduced, the activation energy of local relaxation increased and the relaxation time prolonged respectively.

INTRODUCTION

Polyvinylidene fluoride (PVDF) and copolymers of vinylidene fluoride with trifluoroethylene or tetrafluoroethylene [VDF/TrFE(TeFE)] are typical ferroelectric polymers. Their structural characteristics, ferroelectric phase transitions, piezoelectric and pyroelectric properties have been studied by many researchers^[1-7], but the effects on physical properties with the changes of molecular chain structure are seldom studied. Discussions on the chain structural effect have an important role for further instructing the synthesis of ferroelectric copolymers and investigating thoroughly the properties of copolymers. This paper is intended to take PVDF and VDF(95)/VF(5) as well as VDF(52)/TrFE(48) and VDF(47.5)/TrFE(47.5)/HeFP(5) as

the examples, and to investigate the effect on dielectric physical properties due to the changes of chain structure by 5mol% vinyl fluoride(VF) or hexa-fluoropropylene (HeFP) with the method of dielectric relaxation under the condition of enlarged precision of measuring system.

EXPERIMENTAL

Instrumental

In order to satisfy the measuring needs at low-temperature and low-frequency, we improved the parts of temperature control, sample cell and software of originally commercial and fully automatic system for measuring frequency and temperature spectra of the complex elastic, dielectric, and piezoelectric constants of polymer films^[8] and raised the precision of measuring system from original 1% to 2%. Fig. 1 shows a computer-controlled improved system which is applicable to a broad range of complex dielectric measurement.

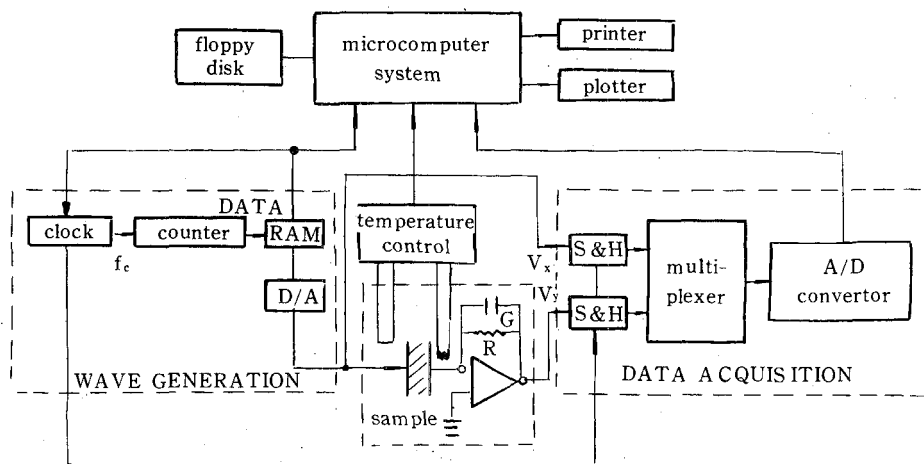


Fig. 1 Block diagram of an instrument system for measuring complex dielectric constants by digital Fourier transform technique

In the measurement, a sinusoidal wave voltage with a well-defined frequency and phase angle is synthesized by means of a quartz clock and applied to a sample. Both the applied voltage and charge response are then sampled simultaneously using the same clock and stored in a microcomputer via a multiplexer and an A/D convertor. By using the same clock for both wave synthesis and signal sampling, it is possible to determine the complex quantities by simple digital Fourier transform, and to store them on a floppy disk or to export them through a printer or a plotter.

Materials

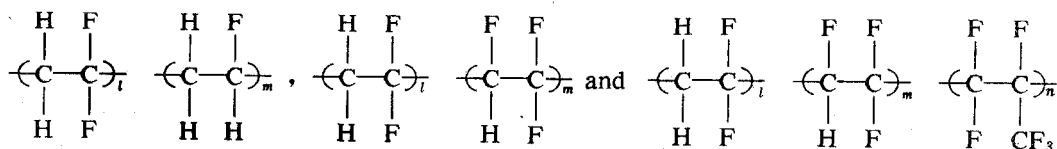
The films of PVDF and VDF(95)/VF(5) as well as the powder samples of VDF(52)/TrFE(48) and VDF(47.5)/TrFE(47.5)/HeFP(5) copolymers were supplied by Kureha Chemical and Daikin Kogyo Co., Ltd., Japan respectively. The films got by crystallizing from the melt are a mixture of crystalline and noncrystalline regions with a degree of crystallinity of 50% approximately^[1]. The thickness is normally 55 μ m.

For powder ones, the film samples with different degrees of crystallinities were prepared by four methods respectively. (1) As-cast samples were cast from methyl ethyl ketone to obtain 30-50 μ m-thick films, (2) Annealed samples were got by heating the as-cast ones at 140°C under vacuum for 2hrs, (3) Quenched samples were obtained by heating the as-cast ones at 180°C and then throwing them rapidly into liquid nitrogen, and (4) Slowly-cooled ones were prepared by slowly cooling the samples from melting state with a cooling rate of 0.5°C/min to room temperature. By using a Cauchy-Cauchy function to fit the X-ray diffraction curves of samples and resolving curves into two peaks, C (crystalline) and N (noncrystalline), the percent crystallinity $X_c = C/(C + N)$ were determined^[9]. X_c of quenched samples is 20%, as-cast ones 30%, slowly-cooled and annealed are about 70-80%, respectively.

Rectangular gold electrodes (23 $\times$ 12mm² in area) were vacuum deposited onto both surfaces of the films. The complex dielectric constants $\epsilon^* = \epsilon' - i\epsilon''$ were measured in the above described measuring system over a frequency range of 10⁻²–10⁴Hz at temperature between -120°C and 140°C.

RESULTS AND DISCUSSION

PVDF consists of a repeat unit CH₂CF₂, which carries a vacuum dipole moment of 7 $\times$ 10⁻³⁰Cm (2 Debyes) associated with positive hydrogen and negative fluorine atoms. The structural formulae of the copolymers are



Because these copolymers are all random ones, we can find from the structure of molecular chain that if 5mol% F atoms in PVDF chains are substituted by H atoms, PVDF will become copolymer VDF(95)/VF(5), and if

5mol% $-\text{CH}_2-$ units are replaced with $-\text{CF}(\text{CF}_3)-$ units, VDF (52)/TrFE(48) will become tercopolymer VDF(47.5)/TrFE(47.5)/HeFP(5). The chain regularity of VDF(95)/VF(5) is lower than that of PVDF. Due to the spatial impediment of 5mol% $-\text{CF}(\text{CF}_3)-$ units, the crystalline properties of tercopolymers will decrease greatly. When measuring Curie point T_c and melting point T_m of tercopolymer (VDF:TrFE = 75:25) by means of DSC, we found that T_c and T_m shifted to a lower temperature region with the increase of HeFP content. When HeFP content exceeded 5mol%, the peak of T_c almost disappeared.

In the frequency spectra of PVDF over a range of $-100^\circ\text{C}-40^\circ\text{C}$, $10^{-2}-10^4\text{Hz}$ (Fig. 2 shows the spectra between -60°C and 0°C), we could observe three types of dielectric relaxation: the crystalline relaxation (high-temperature process) of phase II in a range of lower frequency (α -relaxation), the relaxation of segmental motions (middle-temperature process) of noncrystalline regions in a range of middle frequency (β -relaxation) and that of local motions of small-scale segments (low-temperature process) in a range of higher frequency (γ -relaxation).

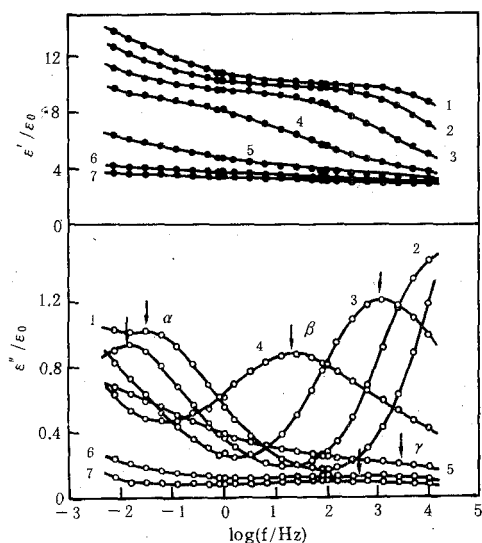


Fig. 2 Frequency dependence of ϵ' and ϵ'' of PVDF at temperature (1) 0°C , (2) -10°C , (3) -20°C , (4) -30°C , (5) -40°C , (6) -50°C and (7) -60°C

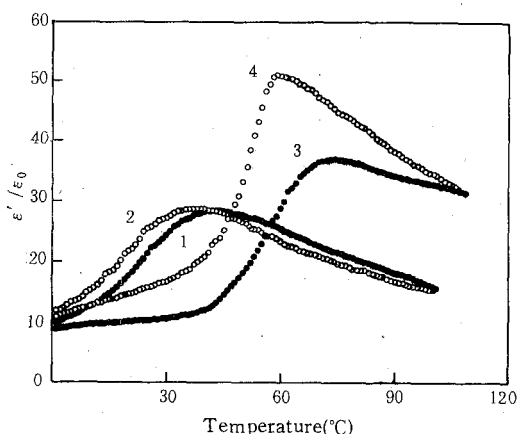


Fig. 3 Temperature dependence of ϵ' for as-cast VDF(47.7)/TrFE(47.5)/HeFP(5) curve (1,2) and VDF(52)/TrFE(48) curve (3,4) copolymers at heating rate of $2^\circ\text{C}/\text{min}$ and 100Hz
● heating; ○ cooling

For VDF (95)/VF (5) copolymer, only β - and γ -relaxation could be

observed, which shifted to low-frequency region with the diminution of temperature in terms of almost the same moving rate as that of PVDF.

Fig. 3 shows the temperature spectra of real ϵ'/ϵ_0 component of complex permittivities for copolymer VDF (52)/TrFE (48) and tercopolymer VDF (47.5)/TrFE (47.5)/HeFP (5) over a temperature range of 0–110°C. It indicates that T_c of copolymer is 70°C (heating process) and that of tercopolymer only 40°C, which is 30°C less than that of copolymer. T_c and ϵ'/ϵ_0 of VDF (52)/TrFE (48) take different values but ϵ'/ϵ_0 of tercopolymer almost takes the same during heating and cooling. For tercopolymer, it is seen only a little of temperature shift associated with temperature inertia, the shapes of spectra during heating and cooling are the same. This suggests that ferroelectric phase transition of tercopolymer has no direct relationship with the thermal history.

In the case of temperature spectra of tercopolymer below room temperature, the glass transition can not be seen from the real component, only one prominent relaxation consisted of crystalline and noncrystalline is observed because of the decreasing of T_c . There is also seen from the imaginary component ϵ''/ϵ_0 of complex permittivities in a region below glass temperature a broader relaxation peak (γ -relaxation) associated with local motions of short segments, but its position is difficult to determine due to the effects of relaxation peaks of crystalline and noncrystalline regions.

The frequency spectra of tercopolymer between 20°C and 50°C in Fig. 4 show a relaxation peak moves rapidly to the low-frequency region with decreasing temperature. Such a similar peak is not found in all the frequency spectra of copolymers of VDF with TrFE or TeFE. Compared the frequency spectra in Fig. 4 with the temperature spectra in different frequencies, we found that it was the crystalline relaxation peaks (here called α' -relaxation tentatively) in corresponding to the T_c transition region shown in Fig. 3.

The frequency spectra of quenched VDF (52)/TrFE (48) below room temperature (the spectra shapes of tercopolymer are similar) indicate two types of relaxation peaks (β and γ), as shown in Fig. 5. As the temperature decreases, β -peak ascribed to the micro-Brownian motions of molecular segments in noncrystalline regions shifts quickly, but γ -peak ascribed to the local motions moves slowly to the low-frequency regions. The moving speed of β -relaxation of tercopolymer is slower, while the one of γ -relaxation is faster than that of copolymer VDF (52)/TrFE (48). In this way, when 5mol% VDF is substituted by HeFP in copolymer chains, the peak of crystalline relaxation is separated out and moves rapidly to the low-frequency region with decreasing temperature. This relaxation is frozen

basically below room temperature.

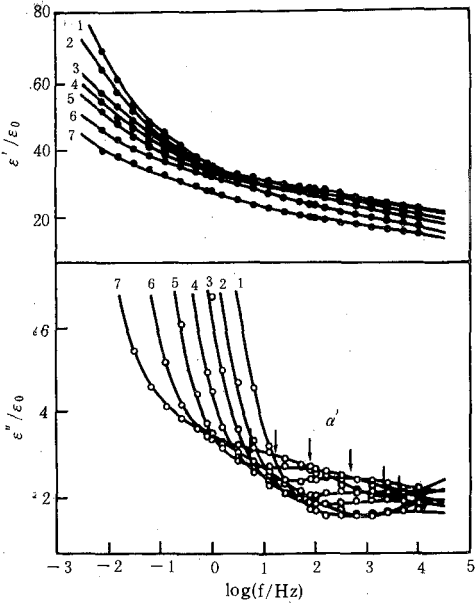


Fig. 4 Frequency dependence of ϵ' and ϵ'' for quenched tercopolymer at temperature (1) 50°C, (2) 45°C, (3) 40°C, (4) 35°C, (5) 30°C, (6) 25°C and (7) 20°C

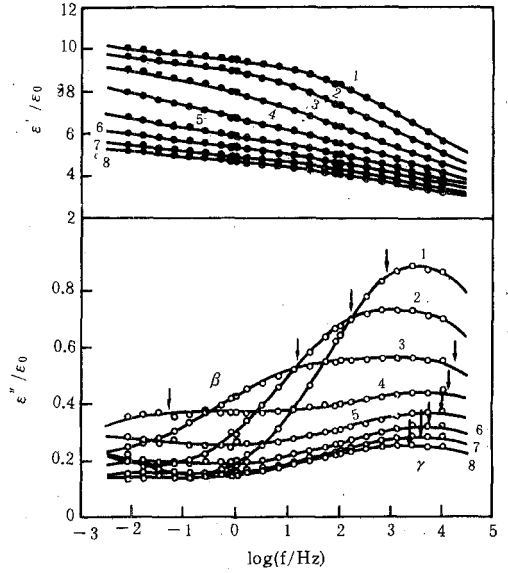


Fig. 5 Frequency dependence of ϵ' and ϵ'' for quenched VDF (52)/TrFE (48) at temperature (1) -10°C, (2) -15°C, (3) -20°C, (4) -25°C, (5) -30°C, (6) -35°C, (7) -40°C and (8) -45°C

In order to separate the relaxation and conduction mechanisms, we tried to reproduce the observed spectra with a microcomputer by using the following empirical function^[10]:

$$\epsilon^*(i\omega) = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^p} + \frac{\sigma}{(i\omega)^q} \quad (1)$$

Where ϵ_∞ is a instantaneous permittivity, $\Delta\epsilon$ is a relaxation strength, τ is a relaxation time and ω is an angular frequency. The p and q are parameters expressing the distribution of relaxation time and dc conductivity.

Six parameters (ϵ_∞ , $\Delta\epsilon$, τ , σ , p , q) of every frequency spectrum were varied so that Eq. (1) could obtain the best agreement with the observed real and imaginary component of complex permittivities. τ and $\Delta\epsilon$ were determined in this way. Fig. 6 shows the logarithm of τ as a function of reciprocal absolute temperature $1/T$ for PVDF and VDF (95)/VF (5) copolymer. The temperature dependence of relaxation frequencies for copolymer VDF (52)/TrFE (48) and tercopolymer VDF (47.5)/TrFE (47.5)/HeFP (5) are shown in Fig. 7. The data of ferroelectric and melting phase transition of PVDF and VDF (52)/TrFE (48) are also shown in Fig. 6 and 7 respectively.

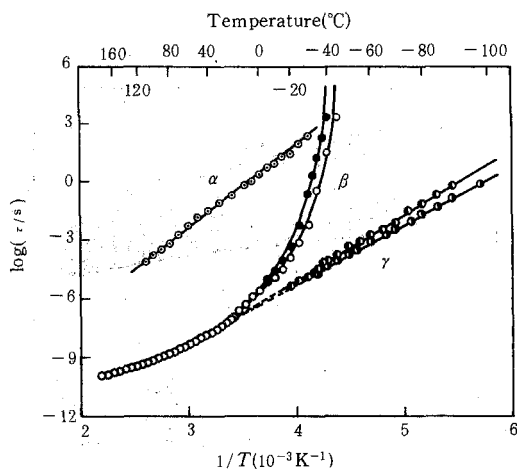


Fig. 6 Plots $\log \tau$ vs. $1/T$ for PVDF (○, ○, ●) and VDF (95)/VF (5) (●, ●) copolymers

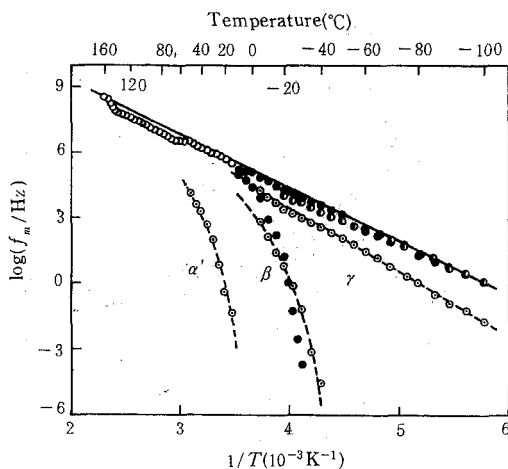


Fig. 7 Transition map of VDF (52)/TrFE (48) (● quenched; ○ slowly cooled; ◐ annealed) and VDF (47.5)/TrFE (47.5)/HeFP (5) (○ quenched) copolymers

The most common polymorph of PVDF crystallized from the melt is the nonpolar phase II which consists of TGTG' molecules packed in an antiparallel fashion^[11], but polymorphic structure of VDF/VF copolymer with small amount of VF is the phase I^[12]. Because α -peaks of PVDF presented in Fig. 2 represent crystalline relaxation of Phase II, there is no α -relaxation in Fig. 6 for VDF(95)/VF(5) copolymer having only the polymorphic structure of Phase I.

In the case of VDF(52)/TrFE(48) copolymer in Fig. 7, the crystalline relaxations near T_c are frozen below room temperature and are transformed into the local relaxation related to the short segmental motions. No any clear boundary appears between the crystalline and local relaxations (we can consider the one above room temperature as the crystalline relaxation). The relaxation process in a noncrystalline polymer occurring above its T_g is associated with a micro-Brownian motion of molecular segments. Its relaxation time is known to follow an empirical WLF equation^[13]:

$$\log \tau(T) = \log \tau(T_g) - \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2)$$

where T is the temperature, $C_1 = 8.86$ and $C_2 = 101.6$ are universal constants. The data of β -relaxation in Fig. 6 and 7 were fitted by Eq. (2) and were found to be in good agreement with it. The fitting results indicate that T_g of VDF(95)/VF(5) is 3°C more than that of PVDF and T_g of tercopolymer is 3°C less than that of VDF(52)/TrFE(48).

It is also seen from Fig. 6 and 7 that $\log\tau$ (or $\log f_m$) of PVDF as well as copolymers lies on a single straight line given by an Arrhenius form

$$\tau = \frac{1}{k_0} \exp(\Delta H/kT) \quad (3)$$

Calculated with Eq. (3), the activation energy ΔH is obtained. The results are shown in Table 1.

Table 1 ΔH of γ -relaxation of PVDF and copolymers

Polymer	ΔH (kJ/mol)
PVDF	58.6
VDF(95)/VF(5)	64.4
VDF(52)/TrFE(48)	46.4
VDF(47.5)/TrFE(47.5)/HeFP(5)	56.5

The linear relation of γ -relaxation of VDF(95)/VF(5) lying over that of PVDF in Fig. 6 shows that the relaxation time of copolymer is longer than that of homopolymer and relevant activation energy is also higher. On account of the diminution of regularity of molecular chain of copolymer, the rotation of dipoles is not so easy as that of homopolymer, thereby the relaxation time goes up. Similarly, the straight line of tercopolymer lying under that of VDF(52)/TrFE(48) copolymer in Fig. 7 also suggests the larger τ and ΔH because HeFP on the molecular chain of tercopolymer enlarges the effect of spatial impediment of dipolar rotations.

Fig. 8 and Fig. 9 show the temperature dependence of relaxation strength $\Delta\epsilon$ of PVDF and copolymers got from the fitting results according to Eq. (1). It can be clearly seen from Fig. 8 that β -relaxation strength of VDF(95)/VF(5) is less than that of PVDF. As a result of the decreasing of F atoms, the amount of dipole moment in noncrystalline regions decreases, thus causes the reduction of β -relaxation strength. In temperature spectra of PVDF and VDF(95)/VF(5) at 100Hz, the peak of dielectric loss of copolymer is smaller than that of PVDF around -20°C , which also proves that β -relaxation strength of copolymer is less than that of PVDF.

The α' -relaxation strength of tercopolymer in Fig. 9 between 20 and 50°C increases sharply with diminishing temperature, and its value is much larger than the ones of β - and γ -relaxations. β -relaxation represents a longer segmental motion in noncrystalline regions, it is restricted by the motion of crystalline regions. HeFP leads to the decreasing of crystallizing ability, the molecular segments are softer, thus β -relaxation strength of tercopolymer is lower relative to that of VDF(52)/TrFE(48). γ -relaxation strength of

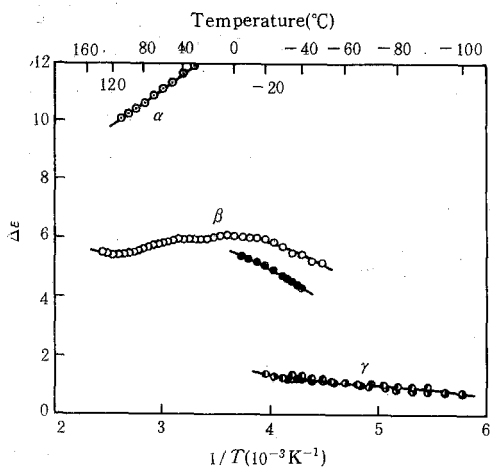


Fig. 8 Correlation of the relaxation strength of PVDF (○, ○, ●) and VDF (95)/VF(5) (●, ●) with temperature

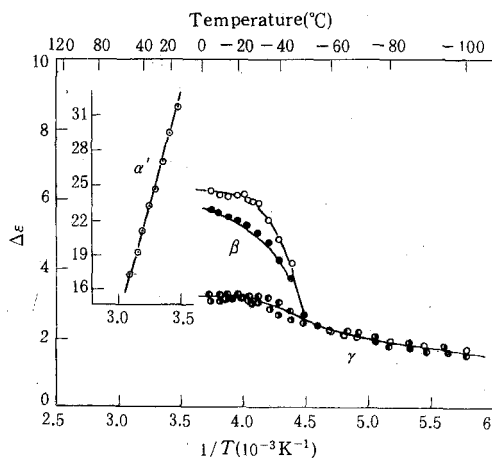


Fig. 9 Correlation of the relaxation strength with temperature for quenched copolymers ○, ●, ● VDF (47.5)/TrFE (47.5)/HeFP (5); ○, ● VDF (52)/TrFE (48)

PVDF and VDF (95)/VF (5) in Fig. 8, as well as that of VDF (52)/TrFE (48) and VDF (47.5)/TrFE (47.5)/HeFP (5) in Fig. 9 are roughly the same separately. This may be interpreted as that the segments of local relaxation are very short, the decreasing or increasing of small amount of F atoms or HeFP can not lead to a great change for γ -relaxation strength.

CONCLUSIONS

1. The crystalline properties and noncrystalline relaxation of PVDF are affected greatly by introducing 5mol% vinyl fluoride into molecular chains. α -relaxation of copolymer VDF (95)/VF (5) disappears, noncrystalline relaxation strength diminishes, T_g increases by 3°C, ΔH of local motion by 5.8kJ/mol and relaxation time goes up.

2. As the vinylidene fluoride is substituted by hexafluoropropylene in the chains of copolymer VDF (52)/TrFE (48) to form the tercopolymer VDF (47.5)/TrFE (47.5)/HeFP (5), the relaxations of crystalline and noncrystalline regions are separated. T_c of copolymer decreases by 30°C and T_g by 3°C, noncrystalline relaxation strength diminishes, ΔH of local motion increases by 10.1kJ/mol and the relaxation time increases.

Keywords:

Polyvinylidene fluoride; VDF (52)/TrFE (48); Chain structure effect; Dielectric relaxation.

REFERENCES

- [1] Lovinger, A. J. , "Developments in Crystalline Polymers—1", Ed. by Bassett, D. C. , Applied Science Publishers, London, **1982**, p. 195.
- [2] Furukawa, T. ; Date, M. and Johnson, G. E. , *J. Appl. Phys.* , **1983**, 54, 1540.
- [3] Iwamoto, T. ; Itoh, T. ; Ando, Y. ; Miyata, S. and Konishi, T. , *Jpn. J. Appl. Phys.* , **1988**, 27, L1969.
- [4] Furukawa, T. ; Johnson, G. E. ; Bair, H. E. ; Tajitsu, Y. ; Chiba, A. and Fukada E. , *Ferroelectrics* , **1981**, 32, 61.
- [5] Lovinger, A. J. ; Davis, G. T. ; Furukawa, T. and Broadhurst, M. G. , *Macromolecules* , **1982**, 15, 323.
- [6] Lovinger, A. J. ; Furukawa, T. ; Davis, G. T. and Broadhurst, M. G. , *Polymer* , **1983**, 24, 1225.
- [7] Furukawa, T. and Wang, T. T. , "The Applications of Ferroelectric Polymers". Ed. by Wang, T. T. ; Herbert, J. M. and Glass, A. M. , Blackie & Son Ltd, New York, **1988**, p. 66.
- [8] Furukawa, T. ; Date, M. ; Ishida, K. and Ikeda, Y. , *Rev. Sci. Instrum.* , **1986**, 57, 285.
- [9] Tajitsu, Y. ; Ogura, H. ; Chiba, A. and Furukawa, T. , *Jpn. J. Appl. Phys.* , **1987**, 26, 554.
- [10] Furukawa, T. ; Date, M. ; Nakajima, K. and Seo, I. , *Jpn. J. Appl. Phys.* , **1988**, 27, 200.
- [11] Hasegawa, R. ; Kobayashi, M. and Tadokoro, H. , *Polym. J.* , **1972**, 3, 591.
- [12] Doll, W. W. and Lando, J. B. , *J. Macromol. Sci., Phys.* , **1970**, B4, 897.
- [13] Williams, M. L. ; Landel, R. F. and Ferry, J. D. , *J. Am. Chem. Soc.* , **1955**, 77, 3701.