Transitions and Relaxations in Poly(trifluoroethylene)

Toshiharu YAGI

*Application Research Department, Chemical Division, Daikin Kogyo Co., Ltd.,
700-1, Hitotsuya, Settsu-shi, Osaka 564, Japan.*

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ABSTRACTS: Transition behavior in poly(trifluoroethylene)(P3FE) was studied (1) by mechanical-relaxation measurements, dealing with the influence of crystallinity, molecular weight, cold drawing, and copolymerization with vinylidene fluoride, and (2) by dielectric-relaxation measurement at various frequencies up to 300 kHz. In P3FE, two transitions have been observed with peaks at 50°C (designated α) and -20°C (designated β) by mechanical-relaxation measurement at 35 Hz. It was found that the α -transition was related to micro-Brownian motion of main chain in the amorphous region, and the β -transition was related to local molecular motion in both the amorphous and crystalline regions.

KEY WORDS Poly(trifluoroethylene) / Mechanical Relaxation / Visco-elastic Relaxation / Dielectric Relaxation / Molecular Motion /

As one of the fluorinated-ethylene polymers, a few studies have been carried out on poly(trifluoroethylene) [P3FE, $-(\text{CF}_2-\text{CFH})_n-$].

Recently, we reported on the preparation and microstructure of P3FE using a high resolution fluorine-19 NMR spectrometer.¹ It was found that the amounts of abnormal head-to-head, tail-to-tail and tail-to-head linkages in polymer chain were very large. The present work is concerned with the nature of molecular motions in P3FE polymers.

It has been widely recognized that mechanical- and dielectric-relaxation studies are available for characterizing both semicrystalline and amorphous polymers. It would be of great interest, therefore, to study the relaxation mechanism of fluorinated-ethylene polymers, since these polymers are semicrystalline and the chemical structure of their repeating units is very simple, since there are no side groups or small special groups in the main chain.

Recently, Choy and his coworkers² reported the relaxation of P3FE for the first time. It was noted that P3FE exhibits two transitions. And it was concluded that the upper transition was associated with large scale motion of the main chain and the lower transition was attributable to the limited motion of a few segments of the frozen main chain. However, the spectrum was not analyzed in detail. Some problems still exist as to the nature of

transitions and relaxations in P3FE because of its complicated solid-state structure. For example, attempts to describe the crystallinity dependence on the transition peaks have not been successful.

P3FE is classified as a highly crystalline polymer similar to other fluorinated-ethylene polymers. But, the crystal form of P3FE has not been established yet. However, there are some reports claiming that the crystal form is hexagonal and that the main chain takes on a helical conformation in crystal.^{3,4}

The present study is concerned with the determination of transition behavior and motions in P3FE, by mechanical and dielectric measurements in the temperature range from -150 to 100°C . This study deals with the influence of crystallinity, molecular weight, cold drawing, and copolymerization on the mechanical properties, and frequency dependence of mechanical and dielectric properties of P3FE polymers.

EXPERIMENTAL

The preparation and microstructure of P3FE were described in our previous paper.¹ The physical properties of the samples used in this study are listed in Table I. Sample A-2 is a copolymer with vinylidene fluoride (VDF). The detailed process of copolymerization is described elsewhere.⁵

Table I. Physical properties of the samples

Sample code	$[\eta]^a$ dl g ⁻¹	R_c^b °C min ⁻¹	sp ^c	X_c^d %	T_m^e °C
A-1-1	5.9	50	1.9905	53	199.4
A-1-2	4.9	Ice water quenched		49	198.0
A-1-3	5.9	0.3		73	203.4
A-1H	2.2	50	1.9930	56	201.3
A-2	4.7	50	1.9657		185.0
A-1D ^f					

^a Intrinsic viscosity in dimethylformamide at 30°C.^b Cooling rate in the molding process.^c Specific gravity at 23°C.^d Degree of crystallinity estimated by X-ray diffraction method.^e Melting temperature measured by DSC.^f Cold drawing sample of sample A-1-1.

The specimens used for mechanical relaxation measurement were films of about 0.06 mm to 0.3 mm thickness molded by heat-press technique. Three specimens with different crystallinities were prepared by changing the time and temperature of the annealing or quenching. The details of the fabrication procedures are given in the third column of Table I.

Sample A-1D was obtained by drawing sample A-1-1 at room temperature and then annealed at 80°C for 5 hours under strain. the draw ratio was about 400%. The mechanical-relaxation measurements were carried out using a spectrometer (Iwamoto Seisakusho VES-2) and viscoelastometer (Toyo-Baldwin Vibron DDV-2) over a temperature range from -120 to 100°C at various frequencies up to 110 Hz and at a heating rate of about 0.5°C/min.

The specimens used for dielectric measurements were heat pressed in circular-sheets of 1.03 mm in thickness and 50 mm in diameter. The cooling rate in the molding procedure was about 50°C/min. Aluminum was evaporated on the specimen surface in high vacuum. Dielectric measurements were carried out by a transformer bridge (Ando-Denki TR-10) at various frequencies up to 300 kHz and over a temperature range from -150 to 100°C.

The degree of crystallinity was estimated by the wide-angle X-ray diffraction method, using a Rigaku-Denki diffractometer.

The melting temperature was measured by a differential scanning calorimeter (Perkin-Elmer DSC-2) at a heating rate of 10°C/min. Aluminum

pans were used as specimen containers and each specimen weight was about 10 mg.

RESULTS

Mechanical Relaxations

The dynamic mechanical data in the temperature regions of -150 to 100°C and at fixed frequency of 35 Hz for each material investigated here are plotted in Figures 1—4. Figure 1 shows the temperature dependence of dynamic tensile modulus, E' , and loss tangent, $\tan \delta$, for three samples of P3FE at different crystallinities. Two transitions were observed as $\tan \delta$ peaks at near 50°C (designated α) and -20°C (designated β). Figures 2, 3, and 4 show the effect of molecular weight, cold drawing, and copolymerization with vinylidene fluoride (VDF) on the mechanical properties of P3FE, respectively.

Dielectric Relaxations

Figures 5 and 6 show the temperature dependence of the dielectric constant, ϵ' , and dielectric loss, ϵ'' , in the temperature region from -150 to 100°C and at different frequencies indicated. Intermediate frequencies are omitted for clearness. Two distinct peaks, α and β , are also observed in the order of decreasing temperature, corresponding to mechanical relaxation data. A rapid increase in ϵ'' observed at a high temperature and low frequency is thought to be due to predominant ionic conductance. Figure 7 shows the transition map of P3FE, which illustrates the logarithm of frequency

Figure 1. Temperature dependence of dynamic tensile modulus, E' , and loss tangent, $\tan \delta$, for three samples of P3FE at different crystallinities measured at 35 Hz: sample A-1-1 (●), A-1-2 (○), and A-1-3 (◐).

Figure 3. Effect of cold drawing on the dynamic mechanical properties of P3FE measured at 35 Hz: sample A-1D (○) and A-1-1 (●).

Figure 2. Effect of molecular weight on dynamic mechanical properties of P3FE measured at 35 Hz: sample A-1H (●) and A-1-1 (○).

Figure 4. Effect of copolymerization with VDF-monomer on the dynamic mechanical properties measured at 35 Hz: sample A-2 (●) and A-1-1 (○).

Figure 5. Temperature dependence of dielectric constant, ϵ' , for P3FE of sample A-1-1.

Figure 6. Temperature dependence of dielectric loss, ϵ'' , for P3FE of sample A-1-1.

vs. reciprocal absolute temperature of loss maximum in mechanical and dielectric measurements.

DISCUSSION

α -Transition

As seen from Figure 1, the magnitude of the α -transition peak is about 1.8 times larger than that of the β -transition peak for the sample A-1-1, and the peak form of the α -transition is sharp and symmetrical. Figure 8 shows the dependence of the maximum value of the $\tan \delta$ for each transition peak on the degree of crystallinity. As seen from Figure 8, the magnitude of the α -transition peak shows a

Figure 7. Loss maximum frequency ($f_{\max}$) plotted against the reciprocal absolute temperature for the P3FE of sample A-1-1. Closed and open circles represent dielectric and mechanical loss, respectively.

Figure 8. Temperature dependence of the maximum value for $\tan \delta$ of the α - and β -transition peaks.

tendency to increase with a decrease in the crystallinity of the sample. This result indicates that the α -transition reflects molecular motion in the amorphous region. On the other hand, the maximum temperature of the β -transition peak is independent of the degree of crystallinity. The large drop of E' can be observed in the α -transition region. Among three samples of P3FE, the drop of E' of low-crystallinity sample (sample A-1-2) compared notably with high-crystallinity sample (sample A-1-3).

Unfortunately, no significant specific-heat change, indicating the glass-to-rubber transition, could be observed even in liquid-nitrogen quenched sample (perhaps the degree of crystallinity is lower than that of sample A-1-2) by DSC measurement. According to Schuman and coworkers,⁶ the glass-to-rubber transition of P3FE occurs at 31°C, as determined by

differential thermal analysis measurement. Furthermore, Lee and coworker⁷ found a change in the slope of heat capacity in P3FE at 40°C, and took this point as the glass-to-rubber transition temperature, T_g . By applying a good empirical rule, $(T_g/T_m)=2/3$, T_g is calculated as 41°C (T_m is taken as 199.4°C from Table I). Therefore, it is speculated that T_g of P3FE may exist between 30 to 40°C. This conclusion is also supported by the chemical structure of P3FE. The glass-to-rubber transition for both polar and unsymmetrical polymers generally shifts to a temperature higher than that for symmetrical polymers. For example, poly(chlorotrifluoroethylene) [PCTFE, $-(CF_2-CFCl-)_n-$] is a polar and unsymmetrical polymer, and the difference in its chemical structure from that P3FE of is that only chlorine atoms are substituted by hydrogen atoms. T_g of PCTFE polymer is about 52°C.⁸

As seen from Figure 1, T_g lies at the foot of the α -transition peak and the temperature difference between T_g and the α -transition peak is from about 10 to 20°C. Therefore, the α -transition is reasonably related to glass-to-rubber transition.

The α -transition peak can also be observed in the dielectric study, as shown in Figures 5 and 6. Owing to ionic conductance, a well-defined α -transition peak could not be observed except as indicated by a few data. A plot of the logarithm of the frequency vs. the reciprocal absolute temperature of loss maximum for α -transition, obtained by dielectric and mechanical measurement, is given in Figure 7. The curve of $\log f_{\max}$ vs. $1/T$ is linear in the limited temperature range from 43 to 75°C, and does not satisfy the WLF equation.^{9,10}

The activation energy of the α -transition, $\Delta H(\alpha)$, was obtained from a plot of $\log f_{\max}$ vs. $1/T$ by use of the following equation

$$\Delta H = -2.303R \, d(\log f_{\max})/(1/T) \quad (1)$$

where R is the gas constant and T is the absolute temperature. The value of $\Delta H(\alpha)$ was found to be about 56 kcal mol⁻¹ (234.3 kJ mol⁻¹) over the limited temperature range from 43 to 75°C. The ΔH value of primary dispersion in PCTFE is 57 kcal mol⁻¹ (238.5 kJ mol⁻¹)¹¹; this value is quite close to that P3FE.

Thus, from these results and discussion, we have assigned the α -transition to the micro-Brownian motion of the main chain in the amorphous region.

β -Transition

The β -transition peak is observed at -20°C by the mechanical-relaxation technique at 35 Hz, and this peak lies, below T_g . The peak form of the β -transition is broad and unsymmetric.

It is generally said that most linear polymers exhibit one or more secondary transition regions below T_g . These transitions are usually assigned to the relaxation of particular molecular motion, such as the movement of side groups, end groups or small groups within the main chain.

As seen from Figure 5, the magnitude of the β -transition peak of P3FE is not sensibly affected by the degree of crystallinity, at least in the crystallinity range investigated here, compared with the α -transition peak. The peak intensity of the β -transition increases slightly with increase in the crystallinity, showing an inverse tendency toward the α -transition. Therefore, it is speculated that the β -transition relates not only to the amorphous region but also the crystalline region. Therefore, the β -transition is divided into two overlapping components associated with the crystal and amorphous regions. The maximum point of the β -transition peak shifts a little to the upper temperature side with decreasing crystallinity of samples.

It may be noted here that the β -transition peak of these samples is not sensibly affected by molecular weight, cold drawing, and copolymerization with VDF, as seen from Figures 2, 3, and 4. Figure 2 shows the effect of molecular weight on dynamic mechanical properties of P3FE at fixed frequency of 35 Hz. As seen from the figure, the molecular weight, and hence the content of the end groups, does not affect the $\tan \delta$ vs. temperature curve. Since P3FE has no side chains (with the exception of a small number of branches), the process should not be attributed to the end groups but to main-chain motions.

As mentioned above, the $\tan \delta$ vs. temperature curve is not symmetrical. According to Hoffman and coworkers¹² the unsymmetrical loss curve observed in the semicrystalline polymers below T_g is due to the superposition of two relaxation mechanisms: one arises in the crystalline region and the other arises in the amorphous region. In such a case, the relaxation loss curve is not affected by the degree of crystallinity to an extent that can be detected. This fact also supports the above speculation that the β -transition

of P3FE relates to the molecular motion for the both crystalline and amorphous regions.

Many polymers exhibit the relaxations associated with the crystal region on the lower temperature side of the peak. Usually, these may be attributed to local molecular motion of main chains in the crystal lattice. In this molecular motion the crystal structure is not affected by the transition. Hoffman and coworkers¹² observed such relaxations in PCTFE, and attributed them to the chain twisting of "chain end" in the crystal lattice. As mentioned above, the "chain end" groups of P3FE molecule do not affect the β -transition. Therefore, it is considered that other kinds of defects cause crystalline relaxation in the β -transition region.

According to Galperin³ and Lando,⁴ the crystal structure of P3FE is very disordered, according to studies made by electron and X-ray diffraction methods. The ¹⁹F NMR results⁵ indicate that the abnormal head-to-head, and tail-to-tail, and tail-to-head linkages are predominant in P3FE molecule. It is considered that these defects remain in crystal lattice as holes, since the van der Waals radius of fluorine is larger to some extent than that of hydrogen, and the C-F bond distance is also to a certain degree longer than the C-H bond distance. Therefore, the crystal of P3FE is thought to contain many crystalline defects. Although the evidence is not as complete as desirable, it is enough to support the belief that these defects cause the crystal relaxation in the β -transition region to a considerable extent.

In the broad-line NMR measurement of P3FE,¹³ a narrow-line component appears at about -60°C and narrows considerably in the temperature region of the β -transition. This indicates the onset of the local molecular motion in the amorphous region.

The β -transition peak can also be clearly observed in dielectric relaxation measurements, as seen in Figures 5 and 6. A plot of the logarithm of the frequency vs. reciprocal absolute temperature of loss maximum for the β -transition is seen in Figure 7. The curve of $\log f_{\max}$ vs. $1/T$ is linear (Arrhenius type). The activation energy of the β -transition, $\Delta H(\beta)$, was calculated as 28 kcal mol^{-1} ($117.2 \text{ kJ mol}^{-1}$), using eq 1. This value seems to be considerably large compared with that of any linear polymer for a secondary transition. The activation energy of the halogenated-ethylene polymers in the secondary transition region is usually 10 to 20 kcal mol^{-1} (41.8

to 83.6 kJ mol^{-1}): for example, $\Delta H(\beta)$ is 18 kcal mol^{-1} (75.3 kJ mol^{-1}) for poly(tetrafluoroethylene) [PTFE, $-(\text{CF}_2-\text{CF}_2)_n-$]¹⁴; $16.8 \text{ kcal mol}^{-1}$ (70.3 kJ mol^{-1}) for PCTFE¹⁵; 12 kcal mol^{-1} (50.2 kJ mol^{-1}) for PVDF¹⁵; 15 kcal mol^{-1} (62.8 kJ mol^{-1}) for poly(vinyl chloride) [PVC, $-(\text{CH}_2-\text{CHCl})_n-$]¹⁶. Therefore, it is speculated that the comparatively large-scale molecular motion, corresponding to this high value of $\Delta H(\beta)$ of P3FE should arise in this β -transition region.

As seen from Figure 5, the dielectric constant, ϵ' , increases rapidly in the β -transition region and shows very large values of ϵ' at room temperature (i.e., below T_g); $\epsilon' = 7.5$ at 22°C and 1 kHz. The dipole moment, μ , of the repeating unit of P3FE is very large and similar to that of other fluorinated-ethylene polymers; μ is 1.63 Debye for the repeating unit of P3FE. The details of the estimation of μ will be discussed in the following section. It is generally said, the large value of ϵ' found in solid polymers is closely related to the large-scale dipole motion in the amorphous region. Therefore, it is difficult to consider that the limited molecular motion of main chain, such as vibrational motions about their equilibrium position, results in a high value of ϵ' at room temperature. The comparatively large scale molecular motion for the local molecular motion is thought to occur in the β -transition region enough to orient the dipole in the electric field, and is different from the cooperative micro-Brownian motion of main chain which is responsible for the α -transition. In the same manner as in ϵ' , the dynamic tensile modulus of P3FE also changes largely in the β -transition region, as seen from Figures 1, 2, and 3. Therefore, we should like to consider that the comparatively large-scale molecular motion for the local molecular motion may occur in an amorphous region in the temperature region of the β -transition.

Another type of P3FE was prepared at about -50°C using an alkylboron as an initiator, so that the amount of head-to-tail structure was proportional to the polymerization temperature. However, the high-molecular-weight polymer was not obtained enough to make the film strong enough for measuring the mechanical properties. This we could not estimate experimentally whether the β -transition was cooperative type or not.

From the above results and discussion, we have tentatively determined that the β -transition of P3FE

is related to the local molecular motion in both the amorphous and crystal regions, and is associated with the comparatively large-scale molecular motion for the local molecular motion in the amorphous region and with the molecular motion due to the crystal defects in the crystal region.

Effect of Cold Drawing

The temperature dependence of mechanical relaxation data of cold drawn P3FE (sample A-1D) is shown in Figure 3. By the cold drawing process, the intensity of the α -transition peak decreases a little and the maximum temperature of peak shifts to the low temperature side, while these properties of the β -transition peak remain unchanged. It is speculated that the decrease in intensity of the α -transition peak is due to the increase in the crystallinity of sample by the cold drawing process.

At times, a new transition peak is observed by drawing process due to the orientation of polymer chain in amorphous region.^{17,18} However, such a peak could not be observed in the cold drawn P3FE polymer.

Effect of Copolymerization

Figure 4 shows the mechanical relaxation data of 3FE-VDF 87.5:12.5 copolymer (sample A-2). In such a polymer composition, the shape of the $\tan \delta$ vs. temperature curve does not change noticeably and resembles that of P3FE from sample A-1-1. The differences are that the α -transition peak is slightly displaced on the low temperature side, whereas its intensity decreases a little, and the β -transition peak is also slightly displaced on the upper temperature side, whereas its intensity remains unchanged. As seen from the figure, a new peak due to copolymerization modification is not observed on

the $\tan \delta$ vs. temperature curve such as the case with PVC.¹⁹

Further Comments on Transitions of P3FE

As mentioned above, two transitions (α and β) were observed in P3FE polymers. The tendency of the $\tan \delta$ vs. temperature curve, observed in the mechanical relaxation study, closely resembles those of the other fluorinated-ethylene polymers, such as PCTFE,²⁰ and poly(vinyl fluoride) [PVF, $-(\text{CFH}-\text{CH}_2-)_n-$].²¹ These polymers exhibit crystal transition on the high temperature side in high crystallinity samples or in single-crystal mats. However, such a peak was not observed in P3FE even for high-crystallinity samples (A-1-3).

The Dipole Moment of a Repeating Unit of P3FE

The chemical structure of a repeating unit of P3FE is similar to trifluoroethane. However, the dipole moment, μ , of trifluoroethane has not yet been reported in the literature. Table II tabulates the bond moment of C-H and C-F, and the dipole moment of fluorinated methanes.¹⁵ It is seen that the effective dipole moment of the $-\text{CF}_2-$ group is similar to that of CF_2H_2 , $-\text{CFH}-$ to CFH_3 , and $-\text{CH}_2-$ to CH_4 . Therefore, thus μ of the repeating unit is 1.96 Debye for PVDF and 1.79 Debye for PVF.

Although this may seem oversimplified, the dipole moment of the repeating unit of P3FE was calculated by assuming a vectorial sum of the bond-moments. There are three conformations in the repeating unit of P3FE, as shown in Figure 9. The value of the C-F bond moment is taken as 1.81 Debye for $-\text{CFH}-$ group and 1.45 Debye for $-\text{CF}_2-$ group, from Table II. μ of the repeating unit of P3FE was calculated as 1.63 Debye for conformations (I) and (III), and 3.25 Debye for

Table II. Dipole moment of fluorinated methanes; inductive effect of fluorine substitution on the bond dipole moment; data taken from ref 14

Compound	Bond moment (Debye)		Total moment of the molecule Debye
	C-H - +	C-F + -	
CH_4	0	—	0
CFH_3	0	1.81	1.79
CF_2H_2	0.23	1.45	1.96
CF_3H	0.32	1.22	1.64

Figure 9. Three conformations of the repeating unit of P3FE. The conformations (I) and (III) are less polar, and conformation (II) is more polar.

conformation (III). The conformations (I) and (III) are less polar and (II) is more polar. Among these three conformations, the steric hindrance of conformation (II) seems to be larger than that of the other conformations. According to the results of the conformational analysis of atactic P3FE by Colda and Lando,⁴ the *trans* conformation is more stable than *TGTG'* conformation. Therefore, the effective dipole moment of the repeating unit of P3FE is approximately 1.63 Debye in practice. As is obvious from Table II, this value is similar to that of trifluoromethane.

Analysis of Dielectric Properties in the β -transition

Figure 10 shows the frequency dependence of ϵ'' for the P3FE of sample A-1-1 at various temperatures. The curves of ϵ'' vs. frequency seem to fit the Cole-Cole equation.²² Figure 11 shows the temperature dependence of the Cole-Cole's parameter β and magnitude of the dielectric relaxation $T\Delta\epsilon$ ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$). T is the absolute temperature. ϵ_0 is the static-dielectric constant and ϵ_∞ is the dielectric constant at a very high frequency at which the orientation of any dipole does not take place. The numerical values of both β and $\Delta\epsilon$ were estimated by Cole-Cole plot. In Figure 11, $T\Delta\epsilon$ was adopted instead of $\Delta\epsilon$ so as to remove any influence of temperature on $\Delta\epsilon$. It is seen from the figure that the value of β increases linearly with increasing temperature in the temperature region shown in the Figure. The result indicates that the distribution of relaxation times increases gradually with increasing temperature. The value of $T\Delta\epsilon$ also increases slowly with increasing temperature in the temperature region of -50 to 0°C . These temperature regions are considered to correspond to the β -transition region of P3FE.

For evaluation of the dipole moment of polymer

Figure 10. Frequency dependence of dielectric loss, ϵ'' , for P3FE of sample A-1-1 at various temperatures.

Figure 11. Variations with the temperatures of the Cole-Cole distribution parameter α and the magnitude of relaxation $\Delta\epsilon T$ in the β -transition regions.

molecules, the Frölich-Kirkwood theory²³ is usually used. According to this theory, the dielectric permittivity is expressed by

$$\Delta\epsilon = \epsilon_0 - \epsilon_\infty = \frac{3\epsilon_0}{2\epsilon_0 + \epsilon_\infty} \frac{4\pi N}{3kT} \left(\frac{\epsilon_0 + 2}{3} \right)^2 g_r \mu_0^2 \quad (2)$$

where N is the concentration of the repeating unit; μ_0 the dipole moment; g_r the Kirkwood reduction factor which is expressed as the average of the spatial orientation; k , the Boltzmann constant; and T , the

Table III. The values of the Kirkwood reduction factor, g_r , of P3FE in the temperature region of the β -transition^a

Temp °C	ϵ_α	ϵ_0	$\Delta\epsilon$	$\bar{\mu}^2$	g_r
-60	2.54	3.65	1.11	0.44	0.16
-38	2.55	4.70	2.15	0.89	0.34
-20	2.80	5.55	3.20	1.06	0.40
-2	3.05	7.15	4.10	2.02	0.76

^a The values of ϵ_α , ϵ_0 , $\Delta\epsilon$, and $\bar{\mu}^2$ are also shown.

absolute temperature. The values of ϵ_α and ϵ_0 were estimated by the Cole-Cole plot, mentioned above. The value of μ_0 is taken as 1.63 Debye for the repeating unit of P3FE. The g_r is calculated assuming that the $\Delta\epsilon$ arise mainly from the dipole orientation in the amorphous region.

Therefore, N is given as follow:

$$N = N_A X_a / M_0 V_s \quad (3)$$

where N_A is the Avogadro's number, M_0 the molecular weight of repeating unit, V_s the specific volume, and X_a the weight fraction of amorphous region. The values of V_s and X_a are taken from Table I. The calculated values of $\mu^2 (= g_r \mu_0^2)$ and g_r are tabulated in Table III together with ϵ_α , ϵ_0 , and $\Delta\epsilon$. From these results, it is felt that the free dipole rotation of P3FE molecules does not occur in the β -transition region, since the g_r value takes on a small value in these temperature regions.

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