effects from spectral decompositions of correlation functions based on classical molecular dynamics simulations. The derived spectral densities constitute temperature-dependent effective harmonic models for the anharmonic systems. The quasi-harmonic potential approximation and the extension to the calculation of normal modes and frequencies proposed here have the advantage, however, that the approximations involved in the calculations can be systematically improved. In a forthcoming paper[20] it is demonstrated that the quasi-harmonic potential approximation constitutes the first term in a series expansion of the classical configurational distribution function in the moments of the distribution; the convergence properties of the expansion are under study for a variety of model systems, including the α-helix. With regard to quantum effects, Friesner and Levy have demonstrated[21] that the quasi-harmonic oscillator model provides an optimized reference system for the evaluation of discretized path integrals from which it is possible to compute accurate quantum mechanical expectation values. The evaluation of statistical thermodynamic quantities for large molecular systems such as biomolecules poses difficult computational problems which requires the judicious application of approximations. For proteins with well-defined conformations, the quasi-harmonic oscillator model provides a very powerful approach for studying the thermodynamics. Applications of the method to the binding of a ligand to a protein[22] and to the study of protein fluctuations[23] are under way.

Acknowledgment. We thank Robert Sheridan and Miguel Zuniga for help with the calculations. This work has been supported by a grant from the National Institutes of Health (Grant GM30580). R.M.L. is an Alfred P. Sloan Fellow and the recipient of a NIH Research Career Development Award. J.N.K. is a Camille and Henry Dreyfus Teacher-Scholar.

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High-Temperature Dielectric Relaxation in α- and γ-Phase Poly(vinylidene fluoride)

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ABSTRACT: The dielectric response of poly(vinylidene fluoride) films and single-crystal mats has been measured from room temperature to the melting point in the frequency range 200–10 000 Hz. Samples studied were α-phase melt-crystallized films, isothermally crystallized films of mixed γ and α phase, and mats of solution-crystallized γ and α phase. For α-phase films, observed decreases in dielectric constant with increasing temperature have been correlated with changes in crystallinity due to melting. Ion removal and annealing are shown to have very different effects on the dielectric behavior, though both involve the same heat treatment. In γ-phase films, the dielectric constant increases with increasing temperature to high values. Single-crystal mats exhibit a crossover from an α-dominated relaxation at lower temperature to γ-dominated behavior at high temperature. Very high values of dielectric constant and loss are obtained from mats and from films crystallized isothermally in an electric field, due to a relaxation of the polar γ crystals near their melting point.

1. Introduction

Poly(vinylidene fluoride), PVF$_2$, is a semicrystalline polymer of more than usual complexity. The molecule is highly polar, and in three of the five crystal structures known to exist, the molecular dipoles are parallel, giving polar crystals and electrically active materials. The structure and properties of PVF$_2$ have been summarized in a recent review of Lovinger.[1] The dielectric properties of the crystal forms are generally very different, although some forms are difficult to distinguish structurally. Further, it is often not possible to obtain samples containing only the crystal modification of interest. Even if this can be achieved, the material is only 50% crystalline, so it is always a composite of crystal and amorphous regions, an inhomogeneous dielectric. The amorphous regions of the polar material normally contain some ionic species, which may be free to move at high temperatures. One last complication is that the molecule normally contains a fraction of head-to-head units that strongly affect the stability of the various crystal forms.

Extensive dielectric studies have been performed on the α phase, which is produced by cooling the melt. Investigators identified two[2,3] and then three relaxations,[4-7] one above room temperature and two below. The high-tem-

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Table I

sample	material	crystallinity[a] % total	% α	% γ	preparation
A	KF1100 film	40.9	39.4	1.5	quenched from melt
B	KF1100 film	42.1	20.3	21.8	crystallized at 172 °C
C	Kynar mat	57.2	47.4	9.8	NaCl doped, 7.3×10^{19} ions/g PVF_2
D	Kynar mat	65.8	39.5 (41.1)	26.3 (24.7)	$CaCO_3$ and $CaSO_4$ doped, 6.0×10^{18} ions/g
E	Kynar mat	60.3	25.9 (31.2)	34.4 (29.1)	NaCl doped, 2.9×10^{19} ions/g PVF_2

[a] Results in parentheses are from IR.

perature relaxation has been related to reorientation of dipoles in the crystalline regions, while the two lower temperature relaxations have been assigned to molecular motions in the amorphous component.[6,7] At high temperatures, anomalously large values of dielectric constant and loss were observed and described as being due to ionic conduction.[7] This was confirmed by the observation of a large decrease in loss upon the application of a dc field at high temperatures for several hours.[8,9]

Further studies at high temperatures and low frequencies[10-12] led to attempts to distinguish between various possible effects of ion motion: dc conductivity, where the ions discharge at the electrodes, and ac conductivity, where the ions form a double layer at the electrodes ("electrode polarization") or at the crystal-amorphous interfaces. This "interfacial polarization" due to differences in ionic conductivity of the phases should be distinguished from the Maxwell-Wagner interfacial polarization which arises from differences in dielectric constant in an inhomogeneous dielectric. Exact theories for inhomogeneous dielectrics require knowledge of the local field and can be applied to aligned lamellar systems or to isolated spherical inclusions of the second phase.[13,14] Detailed theories exist for the ac impedance of homogeneous, isotropic materials containing space charge,[15,16,9] and, not surprisingly, these fit best for the fully molten state.

When the α phase is oriented by drawing[7,17] so that the molecular chains lie in the plane of the specimen film, the crystalline dielectric relaxation is considerably depressed. More detailed study[18] showed that the dipole motion corresponding to this relaxation is along the molecular chain, the chain conformation changing from "up", $TGT\bar{G}$, to "down", $\bar{G}TGT$. Similar sorts of conformational changes have been described for phase transformations.[19,20]

Reports on the preparation and dielectric characterization of unoriented γ-phase PVF_2 have been recently summarized.[21] High-temperature isothermal crystallization from the melt produces films containing γ-phase crystals which do not melt until 198 °C.[22] At temperatures just below the melting point, very large values of dielectric constant and loss ($\sim$1000) were observed at 100 Hz.[23] Large values of dielectric loss had been previously found for a PVF_2 melt,[23] but not such large values of dielectric constant.

Very large values of dielectric constant may be caused by ionic polarization[13] or by some orientation of the polar crystals. Dipolar reorientation may be due to rigid-body rotation of crystals or cooperative motions of molecules that reorient the dipoles while leaving the molecular chain direction unaltered. While no Curie point has been reported for PVF_2, ferroelectric reorientation of β-, phase crystals on poling has been observed,[24] and a dielectric constant peaking at 60 in a vinylidene fluoride copolymer system has been associated with a ferroelectric-paraelectric phase transition.[25] Recent infrared experiments by Tashiro et al.[26] indicate the possibility of an irreversible phase transition from the β phase to the nonpolar γ phase at about 172 °C. The authors suggest the ferroelectric-to-paraelectric transition has been identified since spectral changes are similar to those seen in the copolymer.

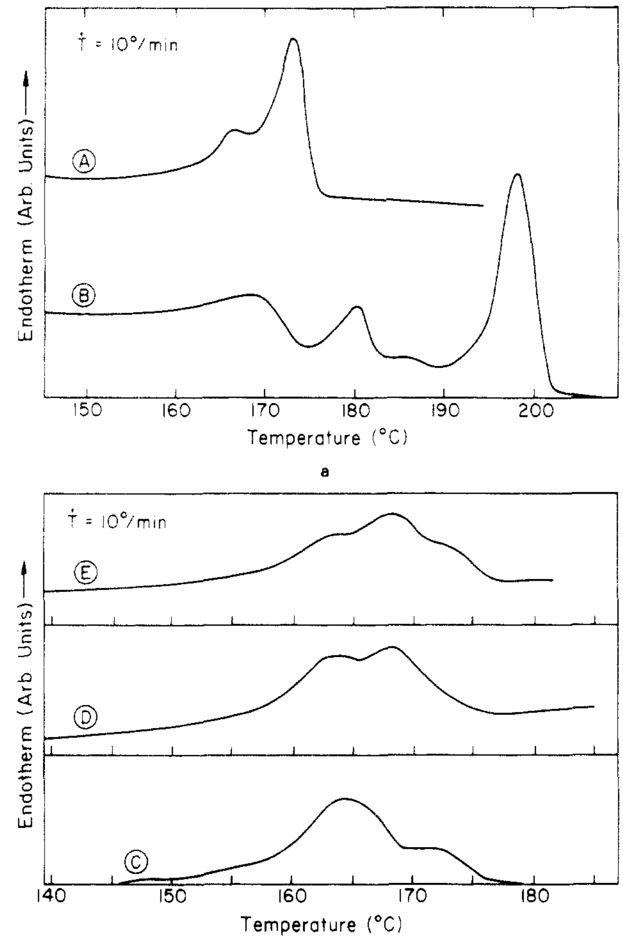
Although the various theories of dielectric properties have specific predictions for frequency and temperature dependence, all assume that one of the many possible loss mechanisms dominates and that the theory for this loss in an otherwise ideal system may be applied to PVF_2. We have used simple tests to determine which class of mechanisms is important in the various specimens we tested. For example, if a large change in properties is observed after ions are removed from the specimen, then the properties before the ion removal are dominated by ion transport. Polarization of the electrodes is most important at very low frequencies and should appear when the crystals, which act as a barrier to ion transport, are completely melted. Differences between samples of similar ion content but different crystalline phases relate to the crystal properties.

2. Experimental Section

2.1. Unoriented Films. PVF_2 films were made from KF1100 polymer supplied by Kureha Corp. Pellets were melted at 220 °C between glass slides and pressed into films about 0.005 cm thick. The films were then quenched in water to room temperature. The film composition and degree of crystallinity were determined by differential scanning calorimetry (DSC). To find the total crystallinity, we assumed that both α and γ crystals had the same heat of fusion, 1.6 kcal/mol.[27] An endotherm for this film is shown in Figure 1a, and film parameters are listed in Table I. Specimen A, containing 39% α-phase and 1.5% γ-phase crystals, received no further treatment. In order to obtain a film with large γ-phase content, specimen B was heated to 215 °C and then isothermally crystallized from the melt at 172 °C, according to the method of Osaki and Ishida.[22] Film B contained 21.8% γ-phase crystals.

Although isothermal crystallization of the melt at 172 °C favored the formation of γ-phase crystals,[22] much of the polymer remained uncrystallized at this temperature. When the specimen was subsequently cooled to room temperature, a large part of this material crystallized as α phase. This results in the broad endotherm below T_c in Figure 1a. The degree of crystallinity of films prepared by this method varied from 36% to 42%. The α-phase content varied from 14.4% to 20.3%, while the γ-phase content remained nearly constant at about 22%. The DSC thermogram for film B in Figure 1a is identical with that shown in Figure 4 of ref 21. In that work, Osaki and Kotaka designate such a film as γ phase, even though a substantial portion of the film is α phase. Using their preparation method, we obtained films with the same DSC thermogram (hence the same relative γ-α content), and all such films contained nearly equal amounts of the two phases. Annealing the specimen at 157 °C improved the total crystallinity but had little effect on the relative amounts of α- and γ-phase crystals. Thus an increase in crystallinity to 54% was accompanied by an increase in both types of crystals, resulting in 29% α phase and 25% γ phase.

2.2. Oriented Single-Crystal Mats. Oriented single-crystal mats were made from Kynar 821 polymer (Pennwalt Corp.) in a dilute solution of a 9:1 mixture of chlorobenzene and dimethylformamide. The detailed method of preparation and characterization has been reported elsewhere.[28,29] Ionic impurities were added to some of the solutions before the crystal mats were precipitated. These impurities caused an increase in the γ-phase



a

b

Figure 1. DSC thermograms, 10 °C/min heating rate: (a) film specimens; (b) mat specimens. Ratio of α phase to gamma phase: (A) 39.4/1.5; (B) 20.3/21.8; (C) 47.4/9.8; (D) 39.5/26.3; (E) 25.9/34.4.

content of the mats. Three such mats used in the present study are listed in Table I. SAXD was used to confirm the orientation of the lamellae with *c* axies normal to the plane of the mat. IR absorption lines at 530 and 510 wavenumbers were used to corroborate the phase content as determined by DSC. In Table I both DSC and IR results of phase content are listed for the high-γ-content mats. As can be seen from Figure 1b, the high-γ-content mats had very indistinct endotherm peaks. Nonetheless, the results of DSC and IR are in close agreement, showing that the mats do contain a large portion of γ-phase crystals which comprise the two highest melting temperature peaks. These results indicate that there has been no recrystallization into a higher melting α form.[30] We found that, in general, the mats melted over a narrower range of temperatures than the films, and the γ-phase melting point in the mats was 177 °C, compared to 198 °C in the films.

In preparation for the dielectric measurement, gold was evaporated onto the surfaces of the specimens to serve as the electrodes. The specimen was placed in an evacuable chamber and immersed in an oil bath. Dielectric measurements were made with a General Radio 1620A transformer ratio arm bridge in the three-terminal configuration at frequencies from 200 to 10000 Hz.

3. Results and Discussion

3.1. Ion-Sweeping Treatment. It is well-known that dc ionic conduction at low frequency and high temperature causes anomalously high values of the dielectric loss.[31] In addition, both constant and loss are affected by ac ionic conduction.[12] In the original work by Osaki et al., [31] a large dc field was applied to the specimen at high temperature for many hours. Ions electroplated as neutral species onto the electrodes and were swept out of the specimen in a process called field cleaning. Another method for the removal of ions involved the application of a dc bias voltage while the dielectric measurements were being made,[11] but at low fields this treatment would merely superimpose a drift velocity on the ions, without altering their energy absorption from the ac field. The dielectric function can be modified by subtracting the contribution due to the ions if this is known.[6,9,10,17] Another recently applied method of ion removal is electrodialysis in water,[32] which was successful in reducing the effects of ions on both the constant and loss.

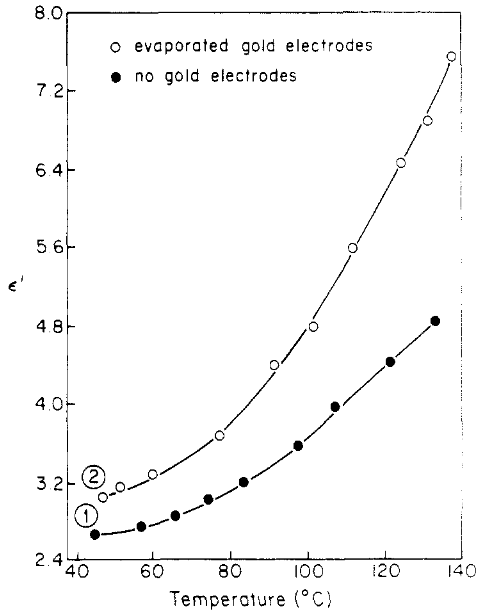


Figure 2. Dielectric constant for high γ content film isothermally crystallized at 172 °C: (1) film surfaces uncoated; (2) surfaces coated with evaporated gold electrodes.

In this work, we minimized the effect of ions by using the field cleaning method. A dc field of about 0.4 MV/m was applied to the specimen at 140 °C for many hours and the film was cooled to room temperature with the field on. Dielectric measurements were taken as the temperature of the specimen was increased. The ion-sweeping temperature was kept below the temperature at which melting started in the DSC (Figure 1). The treatment was effective in reducing dielectric constant and loss for the α-phase relaxation region. For the γ-phase relaxation, which occurs at a temperature above the ion sweeping, the dielectric constant and loss still include the effects of the ions that might be bound in potential traps of higher activation energy. There is no truly satisfactory way of eliminating the effects of ions at high temperatures. The best that can be done is to estimate the magnitude of the ionic contribution and extract the actual constant and loss of the polymer from the data.

Several experiments were done to test the effect of the gold electrodes on measurements of dielectric constant and loss. Figure 2 shows the dielectric constant of a KF1100 γ-phase film before (curve 1) and after (curve 2) the application of evaporated gold electrodes. When electrodes are merely pressed against the specimen, there are many air gaps between the rough specimen surface and the electrodes. An air gap due to surface roughness in the range of 1–5 μm would be sufficient to cause the difference between curves 1 and 2 in Figure 2 by the series capacitance of the air gap. Ion sweeping was completely ineffective when done on an uncoated specimen: experimental data for such a trial would be superimposed on the data

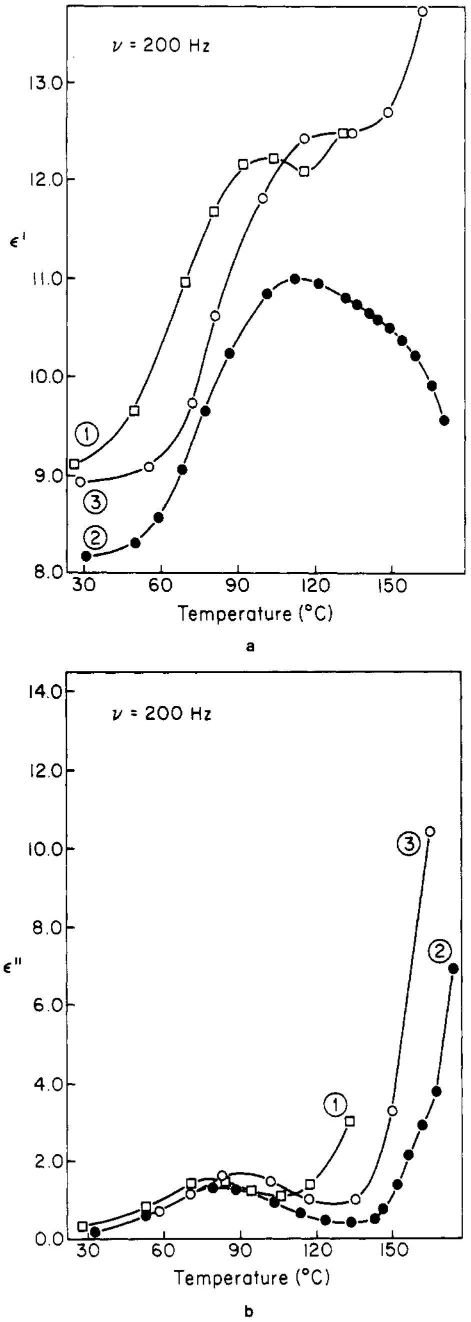


Figure 3. (a) Dielectric constant and (b) loss at 200 Hz: (1) film A before any treatment; (2) film A after ion sweeping at 140 °C; (3) a film similar to A, but annealed at 140 °C.

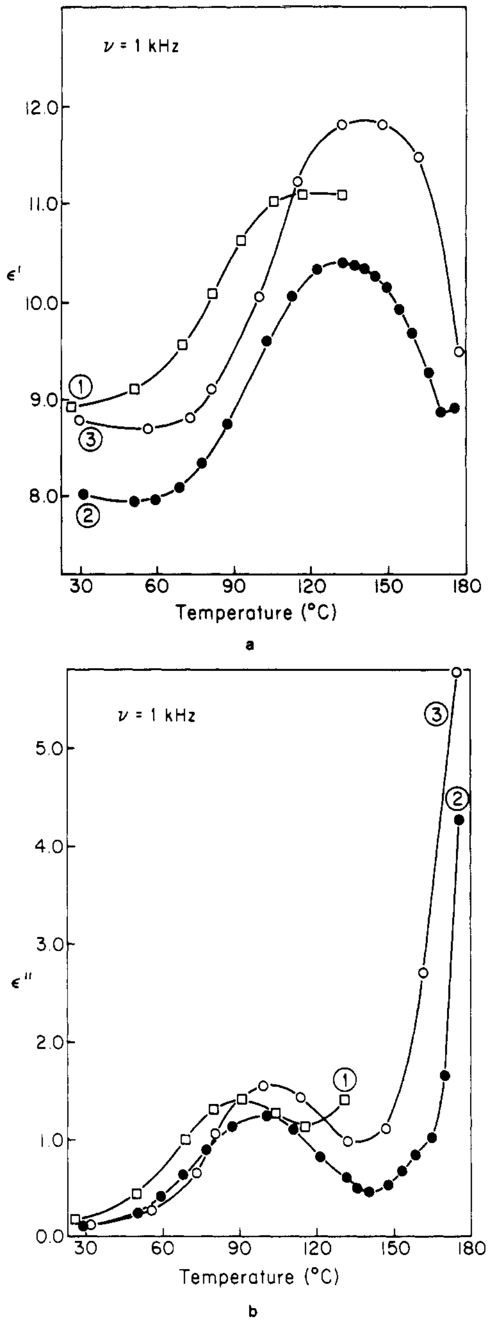


Figure 4. (a) Dielectric constant and (b) loss at 1000 Hz: (1) film A before any treatment; (2) film A after ion sweeping at 140 °C; (3) a film similar to A, but annealed at 140 °C.

in curve 1. This is not surprising, as with no evaporated metal there are relatively few points of contact between film and electrode, and a large resistance to the flow of ions exists across the interface.

Study of the effect of ion sweeping on dielectric properties at high temperature relies on comparing similar specimens, as heating to the high temperature irreversibly changes the material. Up to the ion-sweeping temperature of 140 °C the *same* sample could be compared, before and after treatment. Even at temperatures below 90 °C, where ions are considered to be immobile, we see changes in constant and loss after the treatment. This result indicates that there are other effects of ion sweeping besides ion removal. One such effect is a change in the crystallinity caused by the heat treatment that accompanied ion sweeping. The amount of crystalline phases did alter consistently on ion sweeping, and since the dielectric properties of the different phases are not the same, this has to be taken into account.

To separate the effect of annealing from that of ion sweeping the dielectric response of unoriented α-phase specimens was investigated (1) as prepared, (2) after ion sweeping at 140 °C, and (3) after annealing at 140 °C with no applied field. Results are shown in Figures 3 and 4 and are discussed in detail in the next section. From the shape of the dielectric constant curves it is clear that annealing and ion sweeping have different effects. At low frequency, Figure 3, where the effect of ions is greatest, an annealed film behaves the same way as the film that has had no treatment. As expected, at higher frequency, Figure 4, where ions would be less important, both annealing and ion sweeping give the same result.

3.2. Unoriented α-Phase Films. The dielectric response of α-phase film A is shown in Figures 3 (200 Hz) and 4 (1000 Hz). The loss is the easier to understand. All curves show a peak at 80–100 °C, due to the crystalline

α relaxation. At high temperatures the loss increases due to ionic effects. This is clear since before treatment, curve 1 of Figure 3b and 4b, loss increases rapidly beyond the relaxation peak. It actually begins to rise at 110 °C, but if a symmetric relaxation peak is drawn in, and the excess loss at higher temperatures attributed to ions, they begin to be mobile and effective at 90 °C. Curve 2 of Figures 3b and 4b shows the response after film A had been ion swept at 140 °C for 13.5 h, and curve 3, a similar film annealed at 140 °C with no field applied. Both curves 2 and 3 have high values of dielectric loss at high temperatures, but curve 2 is lower than curve 3 and both are much lower than curve 1 would have been had its testing continued to higher temperatures. (This was done in other experiments, but since here curves 1 and 2 relate to the *same* specimen, curve 1 must stop at 140 °C.)

In the α-relaxation region, the loss peak shows about a 10 °C shift to higher temperature after the treatment for both 200 and 1000 Hz. The enthalpy for this process is about 21.4 kcal/mol and is not sensitive to the field cleaning. This enthalpy is in agreement with that calculated in ref 11. A similar shift in loss peak temperature was seen by Nakagawa and Ishida[6] when the specimen was heat treated at 140–181 °C.

The strength of the relaxation increases in curve 3 and appears to decrease again in curve 2. This depends on the assumed base line curve. Simply taking a common tangent would result in identical peak heights for curves 2 and 3, 50% above that of curve 1 at both frequencies. However, this is not very reasonable, since the "base line" is due to ionic effects that increase rapidly, not linearly, with temperature. Drawing symmetric peaks naturally leaves the peak heights unchanged and gives an ionic loss for the annealed sample, curve 3, beginning at about 100 °C and half that of the unannealed sample. For the field-cleaned sample, curve 2, the ionic loss is not significant until above the ion-sweeping temperature, 140 °C. Uemura[12] also saw decreases in dielectric loss at high temperature and noted that the heat treatment seemed to reduce the effect of the ions.

The dielectric constant, Figures 3a and 4a, is more complicated. The most striking feature observed after removal of ions is the decrease in the dielectric constant at high temperature. The dielectric constant for both frequencies goes through a maximum and then decreases with increasing temperature. The decrease begins below the ion-sweeping temperature for 200 Hz and continues until the specimen is nearly all melted. This decrease is similar to the very slight decrease in dielectric constant observed by Osaki and Kotaka[11] in the unoriented specimen. Both Uchidoi et al.[33] and Furakawa et al.[25] studied the dielectric response of a copolymer of P(VDF–TrFE). This copolymer crystallizes in a conformation similar to that of the polar phase I of the homopolymer of PVF_2. Both sets of experiments report that the dielectric constant reaches a maximum and then decreases with increasing temperature. Uchidoi's results are interpreted as evidence for a phase change to a less ordered structure, while Furakawa and co-workers support the view that the constant decreases because of a ferroelectric-to-paraelectric phase transition. We see the same type of behavior in this film which is nonpolar α phase. Our results indicate that the α-phase film is simply undergoing a change in crystallinity.

If we consider the film to be a two-phase system of highly polarizable crystals in an amorphous matrix, then a decrease in the total crystallinity due to melting would result in a decrease in dielectric constant of the composite. To obtain a simple estimate of the effect of melting, we model the composite as a system of isotropic lamellar crystals of dielectric constant ϵ_c' embedded in a less polarizable isotropic matrix of dielectric constant ϵ_A'. We then calculate the dielectric constant ϵ' of the composite according to the method of Boyd.[14] Changes in ϵ' due to changes in the volume fraction of crystals can then be compared to the data. We used the following assumptions when modeling the composite. (1) At room temperature, well below the crystal relaxation temperature, the properties of the amorphous matrix dominate the composite. (2) Because the amorphous regions have reached their maximum polarizability at a low temperature, the matrix dielectric constant remains fixed as the temperature passes through the relaxation region for crystalline part of the composite. (3) The crystal volume fraction remains constant until about 135 °C when the first crystals begin to melt, an assumption verified by DSC. (4) The polarizability of the crystals reaches a maximum for temperatures above the relaxation region and is unaffected by further heating. Calculations for data at 1 kHz on the basis of these assumptions are as follows:

Table II

T, °C	X_c	ϵ' data	ϵ' calcd
140	0.53	10.4	10.5
153	0.47	9.9	10.2
165	0.35	9.3	9.8
170	0.21	8.9	8.95

1. The dielectric constant of the composite at room temperature is that of the amorphous matrix, so that $\epsilon_A' = \epsilon'(25\ °\mathrm{C}) = 8.0$.

2 and 3. The amorphous properties are constant with increasing temperature and crystallinity X_c is constant at 0.53 up to 140 °C, so ϵ_c is found by using Boyd's formulas[14] for the upper and lower bounds of a randomly arranged lamellar system. In all cases, the upper and lower bounds were very close, so we show only the equation for the upper bound:

$$\epsilon' = (1/3)(\epsilon_v + 2\epsilon_h) \tag{1}$$

where

$$\epsilon_h = (X_c)\epsilon_c' + (1 - X_c)\epsilon_A'$$
$$1/\epsilon_v = X_c/\epsilon_c' + (1 - X_c)/\epsilon_A'$$

Solving for ϵ_c', we find $\epsilon_c'(130\ °\mathrm{C}) = 13.1$.

4. For temperatures above 130 °C, ϵ_c' is constant. With DSC results for $X_c(T)$ all composite parameters are known. Solving eq 1 for $\epsilon'(T)$ gives the variation of ϵ' with crystallinity, shown in Table II.

Table II shows that this model predicts the correct magnitude of the dielectric constant, which decreases as crystals melt. While the model works well by comparison to the data at 1 kHz, it is not totally satisfactory for the lower frequency. The dielectric constant begins decreasing for 200 Hz about 20 °C below the onset of melting, an indication that melting alone is not responsible for the decrease. This composite model also predicts that the dielectric loss should decrease for temperatures above 140 °C. However, an increase in loss is observed and this is taken to be due to ions that were not removed by ion sweeping at 140 °C.

The decline in dielectric constant is thus well explained by melting. Returning to Figures 3a and 4a, we find two other noteworthy features of the dielectric constant behavior. (i) The annealed sample, curve 3, follows that of the ion-swept material at 1 kHz, Figure 4a, but not at 200 Hz, Figure 3a, where it continues to rise at high temperatures. This is easily explained, as low frequencies and high temperatures are the conditions for greatest ionic effects. At 200 Hz, interfacial polarization or other ac ionic effect may dominate the dielectric constant if there are many ions. (ii) The annealing has little effect on the dielectric constant at room temperature, but field cleaning lowers the constant at *all* temperatures. The annealing produces an increase in crystallinity, and that this has little effect on the room-temperature dielectric constant of the sample is a justification for assumption (1) in the calculations above. It is not at all clear why ion removal should reduce the dielectric constant at low temperatures where there is no effect on dielectric loss.

Now that crystallinity changes are known to be important for the dielectric constant, the effects can be seen in the dielectric loss, not in the melting region, but at the α relaxation. One normally expects an increase in crystallinity and crystal perfection on annealing,[6,34] and these should result in a higher dielectric loss at the crystal relaxation and a higher loss peak temperature, respectively. In this case, before heat treatment, film A was 40.5% crystalline, with the least perfect crystals melting at 148 °C. After the treatment, the total crystallinity had improved to 53.2%, an increase of nearly 13%. However, the heat treatment did not change the position of the main melting peak in the DSC, implying no significant increase of crystal thickness or perfection. This result is consistent with annealing studies of melt-crystallized films[6] and of solution-crystallized single crystals[29] of α-PVF_2, where crystals of PVF_2 thickened very little upon annealing below 160 °C. Indeed, after annealing, the DSC shows that crystals begin melting at a lower temperature, about 141 °C, and most of the increase in area of the melting endotherm is below the peak, indicating a reduction of mean perfection. Thus the annealing increases X_c but lessens perfection as judged by DSC, and on this basis we might expect greater loss at the crystalline relaxation and lower peak temperatures. The peak temperatures are higher, and the simplest explanation for this discrepancy is that the crystals produced by quenching in the original film A reorganize to more stable forms during heating in the calorimeter, and the observed peak temperature does not correspond to the perfection of the original crystals.

To summarize this section, we observe that for an unoriented α-phase film after ion sweeping, the onset of melting is accompanied by a decrease in dielectric constant. The magnitude of the decrease in constant is adequately predicted by a model composite medium calculation. Both annealing and ion sweeping cause an increase in relaxation time and a reduction in loss at high temperature. Ion sweeping is much more efficient, delaying the onset of ionic effects until above the ion-sweeping temperature. Annealing increases the α-relaxation loss, due to increasing crystallinity, but ion sweeping reduces it, and it is not clear why this is so.

3.3. Unoriented γ-Phase Film. Film B is an unoriented KF110 film isothermally crystallized at 172 °C. The DSC endotherm for film B has been shown in Figure 1a and indicates a broad low-temperature tail of α-phase crystals which begin melting at 138 °C. The γ-phase crystals have a melting point of 198 °C and constitute about 52% of the crystals in the film. Film B received nearly the same ion-sweeping treatment as film A. The temperature of the ion sweeping was 140 °C, and the duration was 16.5 h. The results for the dielectric response of film B after ion sweeping are shown in Figure 5 for 1000 and 10 000 Hz.

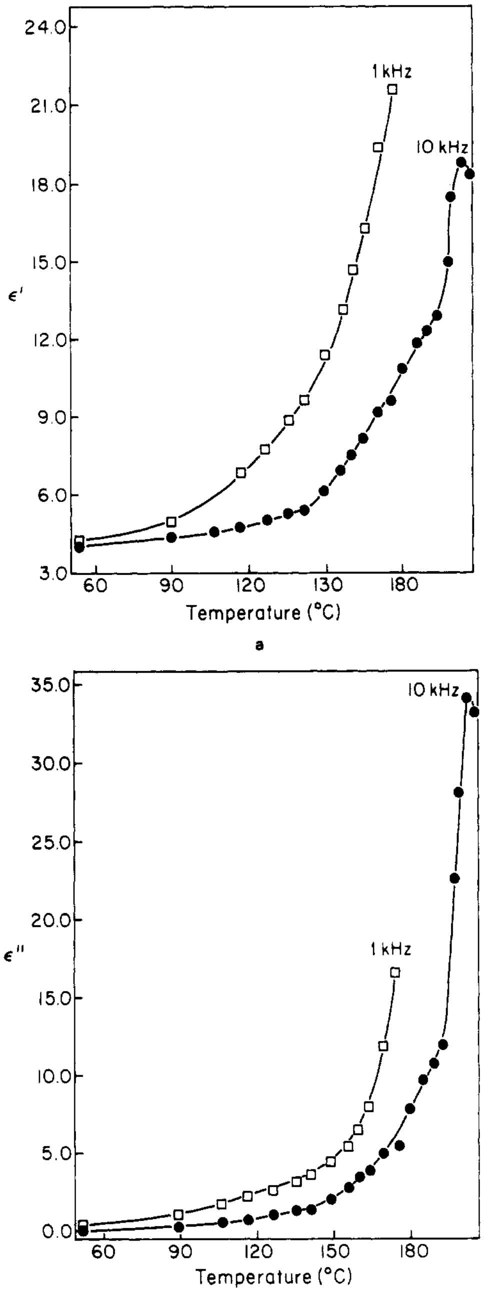


Figure 5. (a) Dielectric constant and (b) loss for a high γ content film B: (●) 10 kHz; (□) 1 kHz.

Comparing film B with film A after ion sweeping and at the same frequency, 1 kHz, the dielectric constant of film B, Figure 5a, is smaller than that of film A, Figure 4a-2, at low temperatures and at the α-phase crystalline relaxation. However, the dielectric constant of film B continues to rise sharply above 130 °C where that of film A is leveling off and falling. The dielectric constant of the α-phase film fell 15% in the temperature range 130–170 °C. Over the same range the increase for film B was from 8.9 to 19.4, a 54% rise. Exact application of the model used in section 3.2 on film A for dielectric constant is not possible in a three-phase system, but qualitatively the melting of half as much α-phase crystals in film B should produce a small decline, so that the increase must be due to the γ phase.

The dielectric loss in the γ-phase film B at 1 kHz, Figure 5b, is about the same as that in the α-phase film A, Figure 4b-2, at low temperatures, but clearly film A has a loss peak and film B does not. It is not clear why there is no α-relaxation peak visible, although there is still a very significant amount of α-phase crystals in the sample. One explanation for the disappearance of the α peak may be that the α and γ relaxations overlap in this temperature range. Both losses rise sharply as the temperature rises above the ion-sweeping temperature, but note the change of scale between the two figures. The loss at 175 °C is 4 times higher for film B. At higher temperatures still, approaching the γ (or γ') melting point of 198 °C, Figure 1b, experimental difficulties prevented the collection of 1-kHz data (losses were too high) but at 10 kHz it is seen that the increase in dielectric constant and loss with temperature becomes more rapid, to give a very sharp increase to high values. When the γ melting point is exceeded, at over 200 °C there is the beginning of a roll over and decline in both constant and loss. Testing an α film at 10000 Hz for comparison gave the same qualitative results as film A at lower frequencies; that is, at high temperatures the loss increased and the constant decreased.

An increase in loss at high temperatures was ascribed to ionic effects in the case of α films, but now constant *and* loss increase, to high values. Since the α-phase and γ-phase films are cast by the same procedure, they should contain the same concentration of ions. If ions are responsible for the rise in dielectric constant at high temperature and high frequency, both α and γ films should show the same response. This is a somewhat simplistic view, since the different melting temperatures of the two phases mean that the films are not exactly comparable at a given temperature. However, the differences in properties are so great that it is not necessary to make the comparison exact. Over a limited range of temperatures we can compare our results to those of Osaki et al.[23] For 10000 Hz the magnitudes of constant and loss are slightly lower than those cited in ref 23. In addition, the loss shows a very steep rise at 10000 Hz, which decreases once the melting point has been reached, whereas Osaki's results for 10000 Hz show a broad flat maximum. These differences may be the result of variations in starting materials, since the number of head-to-head defects and residual impurities can affect values of constant and loss. We do see a maximum in the loss component occurring at about 198 °C, confirming Osaki's result for a relaxation due to the γ-phase crystals.

Our results may also be compared to those of Yano,[10] in which similar large increases in constant and loss were reported. Yano attributed these results to the effects of ions for temperatures near the melting point of the films (which were at lower temperatures, since Yano used a pure α-phase polymer). These conclusions may be less applicable to our situation, since Yano did not ion sweep his specimens. We found the ionic conductivity of the melt to be quite small, making a negligible contribution to the measured dielectric loss. To make a further test of the possible effects of ions on the dielectric constant, electrode polarization effects were calculated with the formulas of Uemura.[12]

Attributing all of the rise in the dielectric constant to ions, we found a self-consistent value for the dielectric loss. In order to make this calculation, we assumed a diffusion constant for singly charged ions of $D = 4.34 \times 10^{-7}$ cm^2/s.[12] The resulting calculated value of the loss needed to account for this effect was 100 times larger than the value we measured. That is, the ionic effect on the constant was much less than that on the loss. Ionic polarization would also predict a stronger frequency dependence than that shown in Figure 5. Thus when the same frequencies are compared, the large values of constant and loss cannot be explained entirely on the basis of electrode or interfacial polarization. We therefore support the very large values for dielectric constant and loss observed by Osaki et al.[23] and their interpretation that there is a very large polarizability of the randomly oriented γ-phase crystals as the temperature increases. Osaki[23] preferred the model of rigid-body motion of the crystals, but it now seems much more likely that the ultrahigh values of dielectric constant are due to the dielectric anomaly of a ferroelectric-to-paraelectric transition. Recent work by Lovinger[35] on copolymers of PVF$_2$ indicates that the existence of a transition is masked by melting. Thus, it seems reasonable that such a transition could exist in polar γ phase, with a Curie temperature near to the melting temperature.

3.4. Oriented Single-Crystal Mats. Oriented single-crystal mats C, D, and E, of Kynar 821 (see Table I), were used in this portion of the study. The total crystallinity of these mats was significantly higher than that of the unoriented films. In addition, the melting endotherms of the mats were quite different, depending on the relative α/γ phase content. As shown in Figure 1b, the mat with the largest α-phase content, mat C, shows two distinct melting peaks, while mat E, having the largest γ-phase content, shows three peaks, including two in the region of the γ-phase melting.[29] The temperatures at which melting occurred were generally lower for the mats than for the films. There are two reasons for this: Kynar material melts at a lower temperatures than KF material[36] and solution-grown crystals are generally thinner and thus less stable than those grown from the melt.

Mat C contains the least amount of polar γ-phase crystals. The dielectric constant and loss after ion sweeping at 140 °C are shown in Figure 6 for low- and high-temperature regimes. Owing to the large α-phase content, we see a distinct relaxation in the region 85–130 °C, depending on frequency. Comparing data at 1 kHz and 120 °C, the dielectric constant of the mat is 74% larger than that seen in the unoriented α-phase film (Figure 4a-2), while mat C contains only 20% more α-phase crystals (Table I). An extra rise in the dielectric constant is to be expected due to the effect of orientation of the c axis parallel to the electric field.[11] The effect seen here is not as large as that seen by Osaki on KF polymer.[11] From Table I it would seem that a more accurate comparison between oriented and unoriented specimens could be obtained from mat D and film A, since they have the same amount of α phase. However, mat D and mat C have almost the same dielectric constant at 120 °C and 1 kHz (Figure 8), and exact comparison is not possible even with mat D as γ-phase material will have some effect at this temperature. The difference between these results on mats and those of ref 11 are most likely due to the different polymer material used. In every case we studied, the Kynar polymer showed smaller values of constant and loss than the KF1100 polymer. Our choice of Kynar for this portion of the study was dictated by the ease with which we were able to obtain different ratios of α phase to γ phase by ionic doping.[29] We were never able to get single-crystal mats of high γ-phase content from KF1100.

Beyond the α-phase relaxation temperature, the dielectric constant of mat C continues to rise sharply, much more like the high γ-phase content film B than the α film A. The increase continues to 158 °C, where at all frequencies tested a decline in dielectric constant begins and continues until about 177 °C. Dielectric measurements are made slowly compared to the heating rates in the DSC. This allows crystals to melt and recrystallize at higher temperatures, so it is reasonable that α-phase melting starts at 158 °C and continues to 177 °C, compared to the DSC melting range of 152–177 °C. Thus just as for the

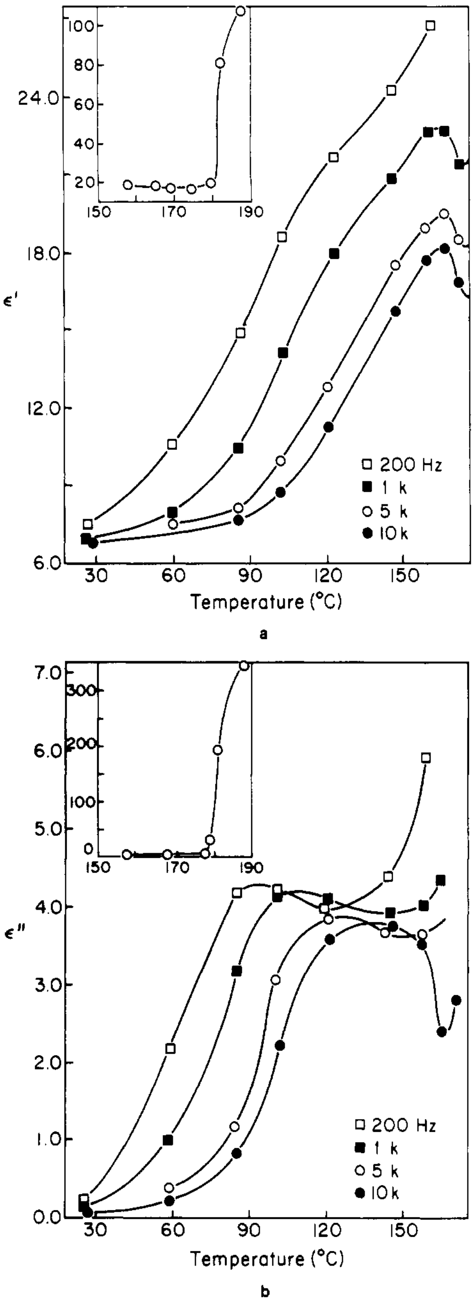


Figure 6. (a) Dielectric constant and (b) loss of a low γ content mat C: (●) 10 kHz; (○) 5 kHz, (■) 1 kHz; (□) 200 Hz.

unoriented α-phase film A in section 3.2, a decline in dielectric constant occurs during melting of α-phase crystals. The decline here is less, about 8% at 1 kHz, although the α-phase crystals are oriented, because other factors—γ-phase material or the larger ionic content—may be tending to increase the dielectric constant. Nevertheless as long as the mat or film contains a significant portion of crystals that melt at low temperature, this melting can be traced through its effect in reducing the dielectric constant.

The fall in dielectric constant between 158 and 177 °C appears twice in Figure 6a, once in the main figure and once in the inset, which shows the high-temperature behavior. The difference in the slopes is due to the differences in scale between the two plots. The rise in dielectric constant at 180 °C and above is thus very steep indeed and the values obtained, ~100, are very high.

The dielectric loss of mat C, Figure 6b, increases rapidly to a peak at the α-relaxation temperature, where its value is 3 times that of film A. However, there is only a slight decrease as the temperature increases beyond the transition, and then the rise continues. This behavior is intermediate between that of the films A and B in the temperature range 130–170 °C. At 1 kHz there is a constant plateau value over a wide temperature range above the α relaxation until at 180 °C where the loss increases very rapidly, reaching a value of 350 at 186 °C (see inset in Figure 6b).

For mat C with large α-phase content we can summarize our results as follows. At low temperature changes in constant and loss are observed that correspond to the onset of absorption by the α-phase crystals and do not seem to be related to ions in the mats. At the α relaxation an increase in constant and loss due to orientation is seen for this single-crystal mat made from Kynar polymer. The γ-phase crystals cause the loss to remain flat beyond the α-phase relaxation over a very large temperature range, from 100 to 160 °C. This is because the γ-phase loss is increasing while the α phase is melting. At the highest temperatures, ions contribute, and as the melting point of the mat is reached, the constant and loss increase steeply.

The dielectric constant and loss for mat E, which has the largest γ-phase content, are shown in Figure 7 for four frequencies. The dielectric constant has the same value at room temperature as it did in mat C, but in the range of the α absorption, the constant is smaller for mat E than for mat C at all frequencies. The dielectric constant continues to rise as temperature increases; there is no drop as seen in mat C. This supports the assignment of that drop to the melting of α-phase crystals. At 170 °C the increase in dielectric constant becomes much more rapid, and the very high values seen in mat C are achieved at a few degrees lower in temperature, in the region where the γ-phase crystals are melting (Figure 1b).

The dielectric loss follows the same pattern of behavior as that of the dielectric constant. Near the α absorption peak, the loss for mat E is about half what it is for mat C, which correlates well with the relative amounts of the two phases present in the mats. This also indicates that the γ crystals are not significantly affecting the absorption near 100 °C, though they are seen to influence the shape of the loss curve at about 130 °C, causing a plateau in absorption for mat E. At 10 kHz, there is no decrease in loss beyond the α relaxation region, such as that seen in mat C. There is instead a reagion of slow increase followed by a region of rapid increase to high values beginning at about 170 °C. As for mat C the constant and loss increase rapidly in the same high-temperature range.

In Figure 8, the dielectric constant and loss for all three mats are shown at 1000 Hz. The general features for the three mats are the same. The dielectric constant curves show that mats C and D are quite similar, in spite of the different types of ionic dopants used in their preparation and doping levels in mat C 10 times that in mat D. On the basis of crystallinity both mats should have larger dielectric constants than mat E, and this obtains until mats C and E cross over at about 165 °C when the α crystals melt. Both mat C and mat E reach very high values at high temperatures (mat D was not tested in this range). Since the rise occurs at lower temperatures in mat E, it has a much larger dielectric constant when mats C and E are compared at the same high temperature.

The dielectric loss, Figure 8b, shows that the resonant absorption due to α-phase crystals is smaller when the α-phase content is smaller. γ-Phase crystal absorption keeps the loss flat beyond the relaxation. Increases in loss at higher temperatures cause a crossover of mats C and E at 150 °C. This ordering is the same as that observed

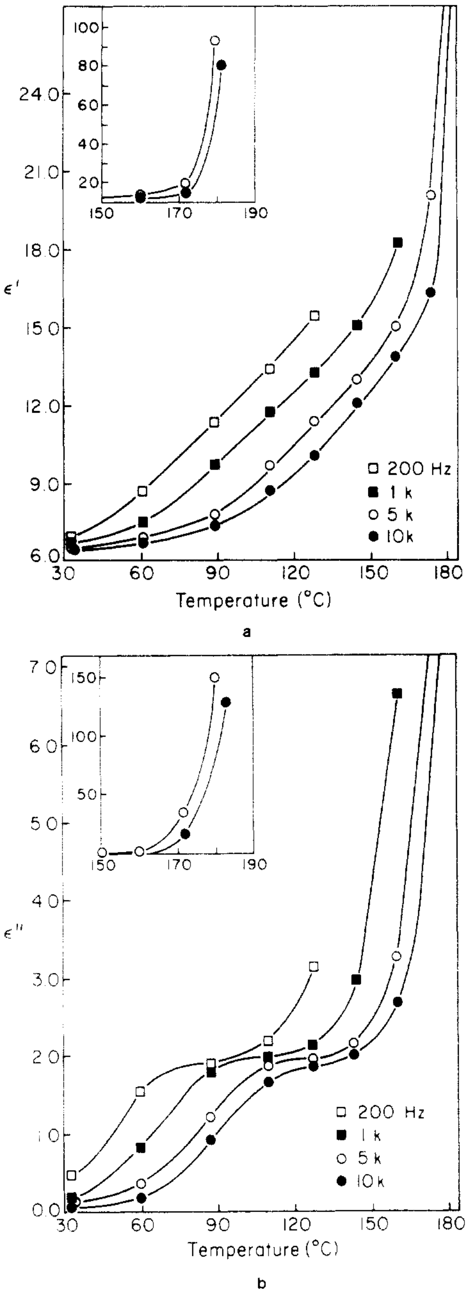


Figure 7. (a) Dielectric constant and (b) loss for a high γ content mat E: (●) 10 kHz; (○) 5 kHz; (■) 1 kHz; (□) 200 Hz.

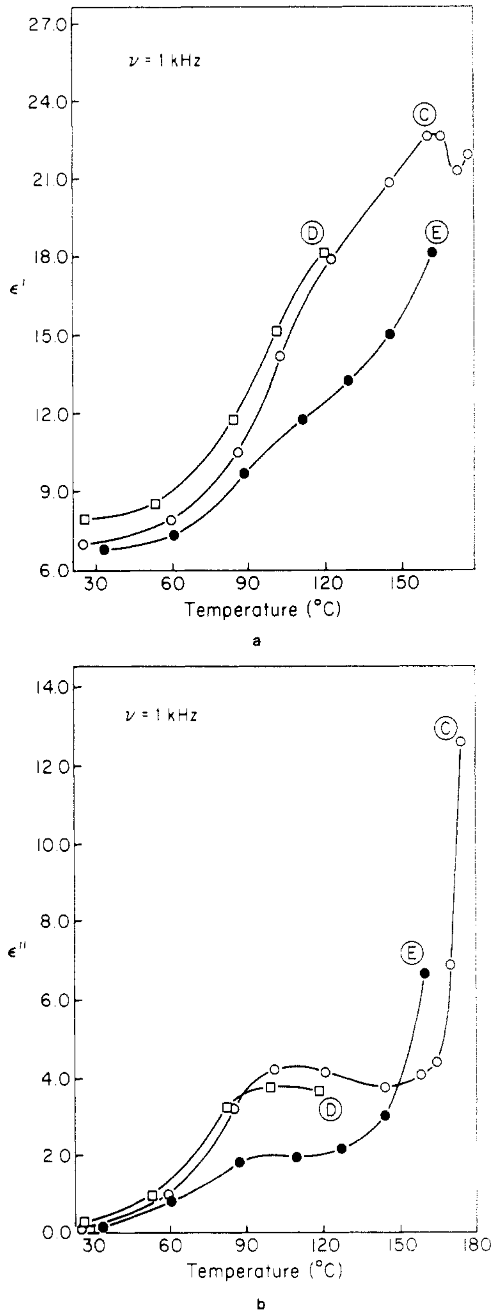


Figure 8. (a) Dielectric constant and (b) loss for a series of mats of varying γ content at 1 kHz. Ratio of α to γ phase: (c) 47.4/9.8; (D) 39.5/26.3; (E) 25.9/34.4.

in the unoriented B and A films. At lower temperatures, α-phase crystals dominated the absorption; above the α-phase relaxation, γ-phase crystals were dominant. At higher temperatures (Figures 6b and 7b) the loss increases dramatically and as for the dielectric constant, the loss of mat E is much greater than that of mat C when compared at the same high temperature. The remaining differences between the mats once the α-phase crystals have melted is the relative γ content (mat E has 3.5 times as much) and the concentration of ionic dopant (mat E has half as much as mat C). This would seem to indicate that the large values of dielectric constant seen here are due to the γ crystals. However, the ionic content listed in Table I is that added to the solution during preparation. In principle, polar γ crystals could attract more ions and cause them to be retained in the solid mat and not be washed away in the mother liquor.

3.5. Causes of High Values of Dielectric Constant and Loss.

In section 3.2 the high values of dielectric constant and loss found for unoriented γ-phase film B were described. They were somewhat lower than those reported by Osaki[11] at the same frequency for a similar preparation (see Figure 9) and were ascribed to an orientational relaxation of dipoles in γ-phase crystals. Ionic effects were ruled out as a major cause of the dielectric properties for the following reasons: (1) The α-phase film A should have the same ionic and impurity content but has a much smaller dielectric constant and loss above 170 °C. (2) Calculation of the electrode polarization effect predicts a much higher value of loss tangent than is observed. (3) The magnitude of the dielectric constant is approximately proportional to 1/(frequency) in the high-temperature region. Interfacial effects would give a stronger frequency dependance.[16] (4) The effects appear around the melting point of the γ-phase crystals independent of frequency.

The solution-crystallized mats C and E were then seen to have much larger values of dielectric constant and loss than film B at much lower temperatures (Figure 9). All solution-grown material contains more ionic contaminants,

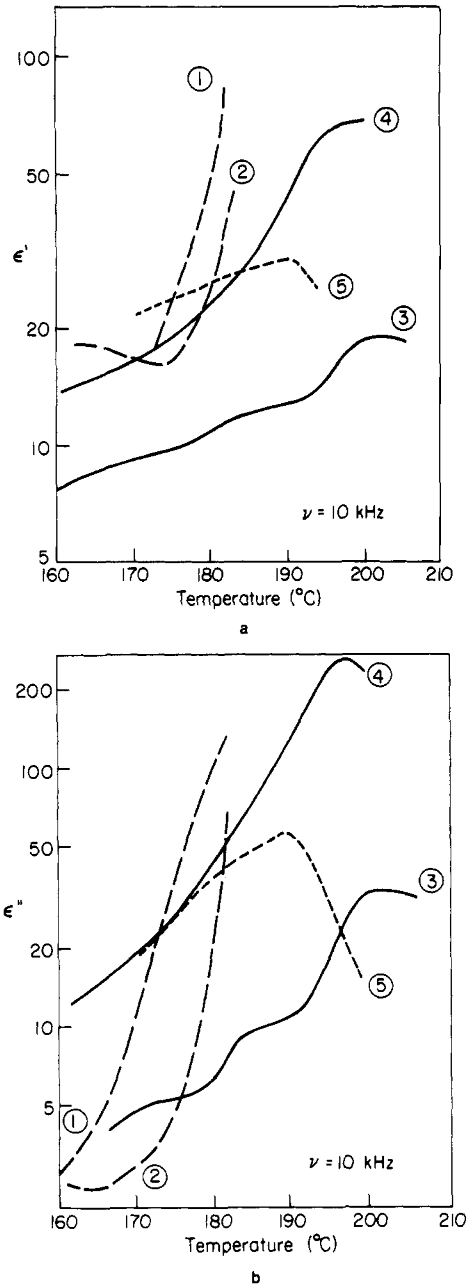


Figure 9. Logarithmic plots of (a) dielectric constant and (b) loss at 10 kHz for a range of sample types: (1) mat E; (2) mat C; (3) γ film B (as in Figure 5); (4) film B after melting and recrystallizing in an electric field; (5) results of Osaki et al.,[23] melt-crystallized γ film.

and in this case large quantities of ionic material were deliberately added. Mat E has more γ crystals than film B, and they are melting where the large values appear, but mat C has little γ-phase content, and DSC measurement, Figure 1b, indicates that the large increases in dielectric constant and loss occur in a region where mat C has completely melted. The simple conclusion from this would be that these high values are associated with electrode polarization and the high ionic content of the mats. As has been mentioned before, the dielectric experiments are very much slower than the DSC heating, and this can affect the melting behavior. When single-crystal mats very similar to mat C were annealed for several hours at temperatures of 160 or 167 °C they partially melted and γ-phase crystals grew from the melt. These γ-phase crystals melted in the region 182–185 °C.[29]

Thus the large values of dielectric constant and loss at 180 °C in mat C could be due to the presence (and melting) of γ-phase crystals that formed during the slow dielectric measurements at 160 °C and above, where much of the α phase had melted. Similar annealing experiments on γ-phase mats showed no appearance of γ phase of higher melting temperature.[29] The melting point of the γ phase is higher initially, and at temperatures where large amounts are melted, the growth rate of new crystals from the melt is very small. It is a general principle that slow heating of less stable material can lead to higher final melting points because the reorganization is more rapid.

This recrystallization to the γ phase would only be considered a possibility, and ions thought to be in some way a major factor in mat properties, were it not for another sample that gave even higher values of dielectric constant and loss. This sample was prepared from film B after it had been electrically tested up to 205 °C, well above its melting point. The molten film was cooled under an electric field of 0.41 MV/m to 167 °C and crystallized isothermally in the field for 20.5 h. It was then cooled and retested. The results are shown in Figure 9, curve 4. The dielectric constant at 10 kHz increased to 65 at 195 °C, well above Osaki's peak of 30 at 190 °C[23] (curve 5, Figure 9), and the loss at the same comparatively high frequency reached 235, compared to 55.[23] The extra processing step increased the constant by 2–3 times and the loss by 4–8 times. This sample has not been described earlier because its phase composition, crystallinity, and orientation are unknown. After preparation in the capacitance cell it was very thoroughly stuck to the electrode assembly. Repeating the preparation did give the same high values of dielectric constant and loss. Later attempts to crystallize in an electric field to give samples for characterization were repeatedly unsuccessful, as the samples tended to short out at such high temperatures. This is clearly a topic for further study, along with extensions to higher fields. The present importance of these specimens crystallized under a field is that they have larger dielectric constant and loss values than found for the mats with no added ions. Indeed the long period under electric field at high temperature should reduce the effective ion content considerably. Isothermal crystallization at this temperature with no applied field produces a mixture of α and γ crystals. Even if the field produces a large increase in the amount of γ phase, it is not possible to explain the threefold increase in dielectric constant on the basis of an increase in volume fraction of a polar component. However, the γ crystals are extremely anisotropic electrically, so some degree of orientation induced by the field could have such an effect.

To check for an orientation effect in the γ phase, we should compare mat E with film B (Figure 5). Meaningful comparisons are very difficult, due to the difference in temperature dependence. Comparison at the same temperature would depend on the temperature chosen and would generally show the mat as having higher values. If the relaxation is close to the melting point, we can try to compare at the same *relative* temperature. Choosing the melting peak temperature from the DSC results, we compare the film loss at 198 °C with the mat loss at 173 °C. In spite of the much higher γ content, the mat has a lower loss than the film.

Conclusions

The apparent dielectric anomaly of reduction of dielectric constant with increasing temperature for the unoriented α-phase samples has been explained as being due to the melting of the crystals over a wide range of temperatures. Other features of the dielectric properties and the effect of molecular orientation are in general agreement with previous work in the field, but some

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puzzles remain, for example, the reduction of dielectric constant at room temperature by ion removal at 140 °C. The availability of pure α-phase samples and the good separation between α-phase effects at lower temperature and γ-phase effects at higher temperature allow one to distinguish the γ-phase properties even when the sample contains both phases.

The γ-phase films show the very high values of dielectric constant and loss previously reported;[23] single-crystal mats show higher values at lower temperatures even when the apparent γ-phase content is small and most crystals have melted. These samples have high ionic contents, so ac ionic effects might be suspected, even at 10 kHz. However, even higher values were found in material crystallized from the melt in an applied electric field, showing that ions are not required for ϵ' and $\epsilon'' > 100$ at 10 kHz. A cooperative relaxation of the dipoles in the polar γ-phase is required for such a strong relaxation, and it is tempting to describe the high values as the dielectric anomaly of a ferroelectric-to-paraelectric transition. However, the crystals are irreversibly melting at the temperature of the relaxation, and this makes such a description somewhat misleading, even if correct, since the transition from order to disorder is always smeared out in polymer crystals.

Acknowledgment. Financial support by the Cornell Materials Science Center, which is funded by the National Science Foundation, is gratefully acknowledged.

Registry No. (Vinylidene fluoride) (homopolymer), 24937-79-9.

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Dielectric Relaxations and Molecular Motions in Homopolymers and Copolymers of Vinylidene Fluoride and Trifluoroethylene

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ABSTRACT: The complex dielectric constant has been measured for homopolymers and copolymers of vinylidene fluoride (VDF) and trifluoroethylene (TrFE) over the frequency range of 1 Hz to 100 MHz at temperatures between −100 and +140 °C. The copolymers show dielectric relaxations associated with a ferroelectric-to-paraelectric phase transition in the crystalline regions. The transition point T_c upon cooling is located near 70 °C. The VDF-rich copolymers show thermal hysteresis in that T_c upon heating is much higher than that upon cooling. Near T_c, the relaxation strength $\Delta\epsilon$ becomes a maximum and the relaxation time τ shows a shoulder. These anomalies and hysteresis are removed by taking the ratio of τ to $\Delta\epsilon$ (the kinetic coefficient) following an Arrhenius-type temperature dependence throughout the transition region. The transition causes changes in the equilibrium permittivity but does not affect the kinetic coefficient. The Arrhenius form of the kinetic coefficient extends well below room temperature, where the noncrystalline relaxation is dominant. This relaxation is analogous to the local relaxation in the TrFE homopolymer but contrasts with the primary relaxation in the VDF homopolymer in the context that the former is of an Arrhenius type while the latter is of a WLF type. It is concluded that the noncrystalline and the ferroelectric relaxations of the copolymers arise from the same type of molecular motions, which basically consist of cooperative trans–gauche transformations.

Introduction

The copolymer of vinylidene fluoride (VDF) with trifluoroethylene (TrFE) has attracted much interest recently because it undergoes a ferroelectric-to-paraelectric phase transition. The transition has been reported to be accompanied by an abrupt increase in crystal lattice spacing, a large increase in dielectric constant, loss of remanent polarization, and an endothermic DSC peak.[2-4] Recent investigations[5-8] have shown that the transition is primarily accomplished by intramolecular conformational changes.

Dielectric relaxations have previously been investigated in the 55/45 and 65/35 copolymers[9,10] revealing the kinetic

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