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The effect of temperature on the structure and dielectric properties of a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene has been investigated at temperatures up to 140 °C. Undrawn or unpoled specimens contain an intimate mixture of two disordered crystalline phases, both of which undergo a large increase in d-spacing at 65-70 °C, with eventual transformation to a single phase in which the chains assume a disordered 3/1-helical conformation above 90 °C. The 70 °C transition is accompanied by a dielectric anomaly. High electric fields applied at temperatures below 70 °C induce a phase change →

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to a single, well-ordered all-*trans* conformation, leading to remanent polarization with piezoelectric and pyroelectric coefficients comparable to those of poly(vinylidene fluoride). The changes in crystal phase and dipole orientation upon poling result in a reduction of the dielectric constant at room temperature, a shift of the dielectric anomaly to ~ 80 °C, stability of the all-*trans* crystal phase to somewhat higher temperatures, and a discrete change in *d*-spacing to that of the disordered 3/1-helical conformation at the transition region. The loss of polarization in poled specimens at this ferroelectric-to-paraelectric transition is attributable primarily to the molecular change from the polar all-*trans* conformation to its non-polar, disordered 3/1-helical counterpart, as well as to the onset of rotational dipolar motions leading to the dielectric anomaly.

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Structural and Dielectric Investigation on the Nature of the Transition in a Copolymer of Vinylidene Fluoride and Trifluoroethylene (52/48 Mol %)

by

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STRUCTURAL AND DIELECTRIC INVESTIGATION ON THE NATURE OF THE TRANSITION IN A COPOLYMER OF VINYLIDENE FLUORIDE AND TRIFLUOROETHYLENE (52/48 MOL %)

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ABSTRACT

The effect of temperature on the structure and dielectric properties of a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene has been investigated at temperatures up to 140°C. Undrawn or unpoled specimens contain an intimate mixture of two disordered crystalline phases, both of which undergo a large increase in *d*-spacing at 65-70°C, with eventual transformation to a single phase in which the chains assume a disordered 3/1-helical conformation above 90°C. The 70°C transition is accompanied by a dielectric anomaly. High electric fields applied at temperatures below 70°C induce a phase change to a single, well-ordered all-*trans* conformation, leading to remanent polarization with piezoelectric and pyroelectric coefficients comparable to those of poly(vinylidene fluoride). The changes in crystal phase and dipole orientation upon poling result in a reduction of the dielectric constant at room temperature, a shift of the dielectric anomaly to ~ 80°C, stability of the all-trans crystal phase to somewhat higher temperatures, and a discrete change in d-spacing to that of the disordered 3/1 helical conformation at the transition region. The loss of polarization in poled specimens at this ferroelectric-to-paraelectric transition is attributable primarily to the molecular change from the polar all-trans conformation to its non-polar, disordered 3/1-helical counterpart, as well as to the onset of rotational dipolar motions leading to the dielectric anomaly.

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INTRODUCTION

The copolymer of vinylidene fluoride and trifluoroethylene containing 52 mol % of the former has been of great interest because it undergoes a ferroelectric-to-paraelectric transition considerably below the melting point of the polymer crystals[2]. The transition has been reported to be accompanied by an abrupt increase in lateral spacing of the chains within the crystal[3], a large increase in relative permittivity[2-7], changes in the relative intensity of infrared absorption bands[5], loss of remanent polarization in D-E hysteresis loops[3,5], and appearance of an endothermic peak in DSC measurements[4,5]. In conjunction with the investigation of the crystalline forms of this copolymer reported in the preceding paper[8], we have obtained additional detailed information on the nature of this transition.

EXPERIMENTAL

The copolymer sample containing 52 mol % vinylidene fluoride and 48 mol % trifluoroethylene was the same as the one used in the preceding study[8], and had been kindly supplied by Daikin Kogyo Co., Ltd., Japan[9]; an experimental sample of polytrifluoroethylene was kindly provided by the Pennwalt Corporation[9]. Polymer films were either extruded or compression-molded from pellets. When mechanically oriented, they had been uniaxially drawn on a tensile testing machine at a constant rate of extension, usually $\sim$4 % /min, at controlled temperatures.

The dielectric constant ($\varepsilon=\varepsilon'-i\varepsilon''$) was measured at 1 kHz as a function of temperature by using a capacitance bridge (Type 1615A, General Radio[9]). The temperature was either increased or decreased at a rate of approximately 1°C/min. Samples were poled at room temperature by applying a maximum dc field of 1 MV/cm as a triangular wave-form of 0.03 Hz toward positive and negative directions for 5-6 cycles. The poled specimens were then cooled to -150°C, and subsequent dielectric measurements were conducted during heating at a rate of 1°C/min.

X-ray diffraction scans were obtained from polymer films at different temperatures using a diffractometer and Cu radiation monochromatized to select the $K_{\bar{\alpha}}$ wavelength. Films on the diffractometer stage were heated electrically from the bottom and the temperature was measured with a thermocouple embedded near the sample; temperatures were calibrated against melting-point standards that had been placed on the top surface of the specimen. Frequently, the gold or indium electrodes on the surface of the polymer served as internal diffraction standards.

Infrared spectra were taken using a Nicolet 7000 Series Fourier-transform spectrophotometer[9] at 2 cm^{-1} resolution with 200 scans in most cases. Heated nitrogen was circulated past the polymer films to vary their temperature.

RESULTS

Poling of our specimens under the conditions described in the experimental section yielded pyroelectric coefficients, p_y, typically around 4 nC/cm^2K and hydrostatic piezoelectric coefficients, d_h, around 20 pC/N, both at room temperature. These values show that the piezoelectric and pyroelectric activity of our samples is comparable to that of poly(vinylidene fluoride). As the purpose of this paper is to examine the phenomena associated with the ferroelectric-to-paraelectric transition at ~70°C, no further piezoelectric data are given here.

(a) Dielectric results. The temperature dependence of ε' and ε'' for unpoled and poled samples is shown in Figure 1. As has previously been described in detail[7], loss peaks are observed in both types of sample at three temperatures, viz. 70°C, -5°C, and -70°C. In this report we are concerned with the process at 70°C, which is associated with a crystalline transition[7]. The relaxation time of this 70°C-process has been found[7] to be 10^{-7} to 10^{-8} sec, so that ε' at 1 kHz represents an equilibrium (low-frequency-limit) dielectric constant, which exhibits an anomaly as shown in Figure 1. Moreover, significant changes in dielectric properties are seen in this Figure as a result of poling. These are: (1) The dielectric constant ε' at 20°C decreases from 16 to 10; (2) Below -50°C, ε' is seen to have increased after poling; and (3) The dielectric peak has shifted from 70°C to 80°C. After being heated to 120°C and thus depoled, these samples show exactly the same dielectric spectra as their unpoled counterparts.

Another aspect of dielectric behavior that was studied in detail involves the depolarization process. Our results are summarized in Figure 2: The poled sample was originally heated to 60°C (solid line from point 0 to point 1), then cooled to 20°C (dashed line from point 1 to point 1'), then reheated to 70°C (solid line 1'→1→2), cooled again to 20°C (dashed line 2→2'), and so on. Although there is slight hysteresis in each of these cycles, ε' is seen in this Figure to return to the same value after each cooling and heating cycle. As the poled sample experiences higher temperatures, the curve of ε' versus temperature approaches the spectrum of unpoled samples and eventually coincides with it above ∿85-90°C. Figure 3 shows a plot of the value of ε' at 20°C against the temperature to which the sample had been heated (i.e., points 1,2, ..., 5 in Figure 2). It is seen that when the sample had been heated to 80°C, ε' rose to the value before poling (i.e., 16) with the most dramatic increase occurring around 65-75°C. Reasons for all of these dielectric phenomena are examined in the Discussion in terms of our results from X-ray diffraction.

(b) Thermally dependent structural changes. When cooled from the melt and not oriented or poled, the copolymer exhibits two closely spaced X-ray peaks at 4.69 Å and 4.59 Å. For reasons outlined in the preceding paper[8], the first of these is concluded to arise from hexagonal (or pseudo-hexagonal) packing of 3/1-helical chains*, and the second from similarly packed trans-planar chains. As temperature is increased to 65°C, the positions and relative intensities of these peaks vary in the manner shown in Figure 4. Both peaks shift to lower angles as the lattice expands thermally; at the same time, the 3/1-helical peak grows at the expense of the all-trans peak as some of the trans-segments begin to transform. Between 65 and 80°C, the peaks are so close in spacing that one appears only as a shoulder of the other. Ultimately, at temperatures between 90°C and the melting point near 160°C, the copolymer exhibits only one narrow peak with an intensity comparable to the combined intensity of the two initial peaks. These changes with temperature are reversible upon cooling, i.e. the two resolved peaks reappear with approximately the same intensity as was observed before heating. The precise variation of lattice spacings with temperature is discussed after presentation of analogous data for unoriented, but poled, specimens.

As has been mentioned in the previous paper[8], poling at

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* As in the preceding paper[8], so here, too, when we refer to 3/1 helical chains we imply a substantially disordered helical conformation; for reasons discussed before[8], both polytrifluoroethylene and the copolymer under study contain molecular defects that cause random departures from the $(TG)_3$ or $(T\bar{G})_3$ conformation of a regular 3/1 helix, as reflected in the breadth and diffuseness of the meridional reflection at ~2.3 Å.

electric fields in excess of ∿500 kV/cm causes the crystal phase consisting of chain-segments in a 3/1-helical conformation to be transformed to a planar zigzag phase. Even those chain-segments already in the *trans*-planar conformation are packed more closely and more regularly by the action of the field, as evidenced by a single X-ray peak,(see Figure 5), displaced to larger angles[8] than either of the peaks in Figure 4 for comparable temperatures. The thermal expansion of this polarized lattice is seen in this Figure to be much smaller than that of the unpoled phases. Between 65 and 70°C, there is a large decrease in the intensity of the all-*trans* peak which is situated near $2\theta = 19.5°$, accompanied by appearance of a second peak near $2\theta = 18.5°$ that corresponds to the 3/1-helical phase. As temperature is further increased, the all-*trans* peak decreases in intensity with little change in position, while the 3/1-helical peak increases in intensity and moves to smaller angles consistent with the thermal expansion displayed by the unpoled polymer. Upon cooling to room temperature from 100°C, two resolved peaks at 4.69 Å and 4.59 Å, typical of the unpoled polymer of Figure 4, are observed; this agrees with the previous evidence[8] in which meridional X-ray reflections were also considered. However, if depoling is performed electrically rather than thermally, i.e. by reducing the remanent polarization to zero through reversal of the electric field to an appropriate value, the single peak at ~19.5°, characteristic of the well-ordered all-*trans* phase, survives.

Thermally induced changes in lattice spacings described above are summarized in Figure 6 and compared with data for polytrifluoroethylene homopolymer which exhibits only the 3/1 helical chain conformation.[8,10] The solid lines pertain to data from the unoriented and unpoled copolymer, the smaller of two spacings at a given temperature arising from the disordered planar-zigzag phase. While similar data have been reported previously[3], one can see here that both of the coexisting phases undergo a large change in intermolecular spacing between 65 and 80°C. Many more data points than are shown in Figure 6 were taken at closely spaced temperature intervals in the region of the transition, so that we are reasonably certain that both phases undergo a transition as indicated by the drawn lines, and not that the curves for the two phases intersect each other around 70°C. This conclusion is further supported by the data from trifluoroethylene homopolymer, shown as the dashed line at the largest spacings in Figure 6. This homopolymer crystallizes only in the 3/1-helical conformation[8,10], and its lattice spacing as a function of temperature coincides with the values from the 3/1-helical segments of the copolymer at corresponding temperatures above 70°C. At lower temperatures, the smaller values of 3/1-lattice spacing for the copolymer compared to polytrifluoroethylene reflect closer packing facilitated by presence of planar-zigzag sequences in disordered chains.

Lattice spacing as a function of temperature for poled (mechanically unoriented) polymer are also shown in Figure 6, where they are the lowest in magnitude, reflecting the improved packing order in these all-trans specimens; this is consistent with the sharpening of all reflections seen in photographic X-ray patterns (preceding paper[8]). The closer packing results in a much smaller thermal expansion, and allows the well-ordered all-trans conformation to persist to higher temperatures than were observed in unpoled specimens. The second peak for poled samples, first seen at 70°C in Figure 5, falls on the curve assigned to the 3/1-helical conformation in Figure 6. This transition behavior differs from that of unpoled samples in that there is a discrete jump in lattice spacing accompanying the all-trans to 3/1-helical transformation, rather than a continuous expansion of two pre-existing lattices. Eventually, at temperatures above ~90°C, the copolymer exhibits only peaks characteristic of the 3/1-helical conformation. These changes will be discussed after presentation of our IR results.

(c) Infrared results. Infrared spectra were examined over a broad temperature range as an alternative means to elucidate the nature of the transition. In poly(vinylidiene fluoride), an absorption band near 510 cm^{-1} has been assigned to a $-CF_2$ bending mode within TTT segments of the chain[11,12]; this band shifts to ∿530 cm^{-1} for the $TGT\overline{G}$ conformation[11,12]. The copolymer investigated here exhibits an absorption band at 506 cm^{-1} that we initially considered characteristic of TTT segments; such attribution has also been made by Yamada et al.[5] for a band observed at 510 cm^{-1} (presumably the same as our 506 cm^{-1} band). However, as shown in Figure 7a, this band does not shift in wavenumber as the sample is heated to high temperatures, at which the X-ray data show that only the 3/1-helical (i.e., $(TG)_3$) conformation is present. This apparent contradiction arises because the exclusive assignment of the 506 cm^{-1} band to TTT segments within the copolymer is incorrect: as shown in Figure 7b, this band is also present in trifluoroethylene homopolymer, which adopts solely the 3/1-helical conformation. At the highest temperatures shown in Figure 7a, black-body radiation from the sample increased noise in the region of low wavenumber; additional experiments to improve the signal-to-noise ratio were not pursued, since it is clear from Figure 7 that these IR spectra do not allow unequivocal interpretation. In general, we conclude that IR evidence in this spectral region cannot be applied as fruitfully as X-ray diffraction to study changes that accompany the transition in this particular copolymer.

DISCUSSION AND CONCLUSIONS

As has been described above and in ref. 8, application of high electric fields induces a phase change in 3/1-helical molecules (non-polar) to the all-*trans* conformation (polar). Poling also causes the *trans*-planar chains to pack more closely and orients the dipoles preferentially in the direction of the field[13-15]; the resultant polarization leads to piezoelectric and pyroelectric properties[13].

These changes in structure and dipole orientation are reflected in the dielectric properties of the copolymer. The most striking of these is the reduction of ε' (measured at 20°C) from 16 to 10; this represents a much greater change than is seen in poly(vinylidene fluoride). The value for ε' at 20°C consists of the full contribution of micro-Brownian motions of non-crystalline segments[7] (-5°C process) plus a partial contribution of the crystalline transition[7] at 70°C (see, again, Figure 1). The more highly ordered all-*trans* phase that results from poling has a smaller lattice spacing and temperature coefficient, and is, therefore, presumed to be dielectrically less active. Hence, the crystalline contribution is reduced in poled specimens, thus explaining the measured decrease of ε' to ~10.

The second effect of poling on dielectric behavior of our samples is the marked increase of ε' below -50°C, leading to a cross-over of curves in Figure 1. This may be the result of several factors: (1) The poled specimens exhibited warping and wrinkling and possibly a decrease in film thickness due to the poling. A decrease in thickness would increase the capacitance and the apparent ε' of the poled film. (2) The poled specimen has only *trans* conformations and the planes defined by the CCC atoms of the polymer chain are preferentially aligned perpendicular to the surface of the film. If the atomic and electronic polarizabilities (the origin of ε' in this temperature range) were greater parallel to the CCC plane than perpendicular to it, ε' for the poled *trans* molecules could exceed that for either randomly oriented trans or 3/1 helical conformations. Such anisotropy in polarizability has been reported for several alkanes (16); halomethanes were less anisotropic. (3) The phase changes occurring during poling might result in a density increase for the sample and hence an increase in ε'. The calculated density of crystals with trans chain conformations is greater after poling than before poling but the conversion of crystals with 3/1 helical conformations to the all trans conformation results in a decreased density. Changes in degree of crystallization were not determined.

The final manifestation of poling is the increase by 10°C of the appearance of the dielectric anomaly (see Figure 1). This is a consequence of the survival of well-ordered all-trans molecules to higher temperatures than in unpoled samples (see Figure 6); the fact that, upon cooling, the dielectric peak shifts down to 70°C is consistent with reversion to a mixture of disordered phases rather than to the original all-trans structure.

At this point, we discuss the implications of our X-ray results for the nature of the transition in the vicinity of 70°C. The various curves of lattice spacing versus temperature (Figure 6) show that the manner in which this transition is described depends upon the chosen frame of reference. Specifically, it is clear from Figure 6 that, when viewed over a broad range (i.e., from 60 to 90°C), the transition is essentially conformational in nature: all specimens eventually end up in the non-polar 3/1-helical phase, irrespective of whether they originated as a mixture of disordered phases (unoriented and unpoled samples), as the well-ordered planar-zigzag phase (drawn samples), or, finally, as the macroscopically polar all-trans phase (poled samples). Over this broad range, therefore, this ferroelectric-to-paraelectric transition deviates from the usual Curie-point phenomenon, inasmuch as loss of polarization is intramolecular through transformation from a polar to a nonpolar conformation.

Within a narrower frame of reference, we may enquire about the nature of the changes occurring specifically in the region of rapid lattice expansion between 65 and 70°C (see,again, Figure 6). A major reason for this expansion undoubtedly lies in the packing requirements of the emerging 3/1-helical conformation. In trifluoroethylene homopolymer, the 3/1-helical lattice is seen in Figure 6 to expand uniformly in the temperature region of the transition. However, in the copolymer the 3/1-segments exhibit initially smaller spacings than those of polytrifluoroethylene, and require the rapid lattice expansion at 65-70°C in order to reach the higher values. This behavior may be accounted for by differences in chain regularity along a given copolymer molecule, which would tend to cause some parts of it to adopt a trans-conformation and others a helical one; the trans segments of neighboring chains would then force the helical segments of the same chains to be packed more tightly. In the same manner, the helical segments are considered responsible for expanding the lattice of planar-zigzag regions in unpoled specimens to larger spacings than are seen in the all-trans phase obtained after poling. This behavior would be analogous to the effect of amorphous surfaces on the lattice spacing of polyethylene crystals[17,18], for which it was found that this spacing decreases with increasing lamellar thickness.

At the temperature where the trans-segments begin to transform to the helical conformation (i.e., ∿65°C), the constrained 3/1 helices will be more free to increase their lattice spacing, thus approaching the packing of polytrifluoroethylene molecules. Because of the disordered nature of unpoled and undrawn specimens, these changes in lattice spacing are continuous, so that intermediate spacings are obtained at temperatures between ∿65 and 70°C. At the same time, the disordered trans-segments in the copolymer will also be undergoing conformational changes to the 3/1-helical phase; however, because these changes are not completed before ∿90°C, intermediate packing distances for the remnants of planar-zigzag segments will be seen up to that temperature.

On the other hand, in poled samples the well-ordered all-trans structure shows a much smaller expansion than its unpoled counterparts, and also survives to higher temperatures (see Figure 6). When the 3/1-helical peak appears, it does so at a spacing characteristic of the trifluoroethylene homopolymer. This shows that in poled samples the transformation occurs in a rather discrete manner from the initial to the final crystalline state, without assumption of intermediate lattice packings. Finally, drawn, but not poled, specimens show similar thermal behavior to that of undrawn, but poled, samples; here, too, the d-spacings shift discretely from small values characteristic of the well-ordered all-trans phase to spacings associated with the 3/1-helical phase of trifluoroethylene homopolymer.

Moreover, our dielectric results reflect another aspect of the transition in addition to the aforementioned conformational change: this is the onset of thermally activated rotational motions in the crystalline regions. According to the previous study of the dielectric behavior of this copolymer[7], the characteristic time constant for orientational relaxations in this temperature range is of the order of 10^{-7} to 10^{-8} s. For such relaxations to be dielectrically active, they should involve corresponding rotational motions of dipolar groups; the latter are associated with the polar trans-segments that are linked by non-polar 3/1-helical groups. Evidence for both conformational and rotational aspects of the transition is seen, and it may be that one triggers the other, although it is not clear at this stage which of the two does so.

In conclusion, our results indicate that the variety of phenomena observed as the copolymer is heated through the transition region reflect the conformational change to the disordered 3/1 helix similar to polytrifluoroethylene, the associated packing rearrangements, as well as the onset of molecular motions. The transition details depend upon the original state of the specimen: drawn or poled samples can shift directly from a well-ordered all-trans structure to the 3/1-helical phase, while the disordered mixture of phases in undrawn and unpoled specimens undergoes continuous, gradual lattice changes to the final helical structure.

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FIGURE CAPTIONS

Figure 1: Temperature dependence of ε' and ε" at 1 kHz for unpoled samples (open circles) and poled samples (filled circles).

Figure 2: Change of ε' of poled copolymer during heating and cooling cycles. Dashed line (open circles) indicates the cooling process, and solid line (filled circles) the heating process.

Figure 3: Change of ε' at 20°C as a result of heating of poled copolymer.

Figure 4: X-ray diffractometric scans from unoriented, unpoled copolymer films at various temperatures. The diffraction angles are those for $CuK_{\bar{\alpha}}$ radiation (λ=0.15418 nm)

Figure 5: X-ray diffractometer scans from unoriented but poled copolymer films at various temperatures. The diffraction angles are those for $CuK_{\bar{\alpha}}$ radiation (λ=0.15418 nm).

Figure 6: Variation of intermolecular spacing with temperature for various samples: ● ———, unoriented, unpoled copolymer; o ·····, unoriented, poled copolymer; Δ -----, polytrifluoroethylene. Data points indicated by ▲ were obtained upon cooling from the highest temperature; all other data points were obtained upon heating.

Figure 7: (a) Infrared spectra of copolymer samples at a series of temperatures. Spectra for elevated temperatures have been displaced vertically for clarity.
(b) Infrared spectrum of polytrifluoroethylene at room temperature.

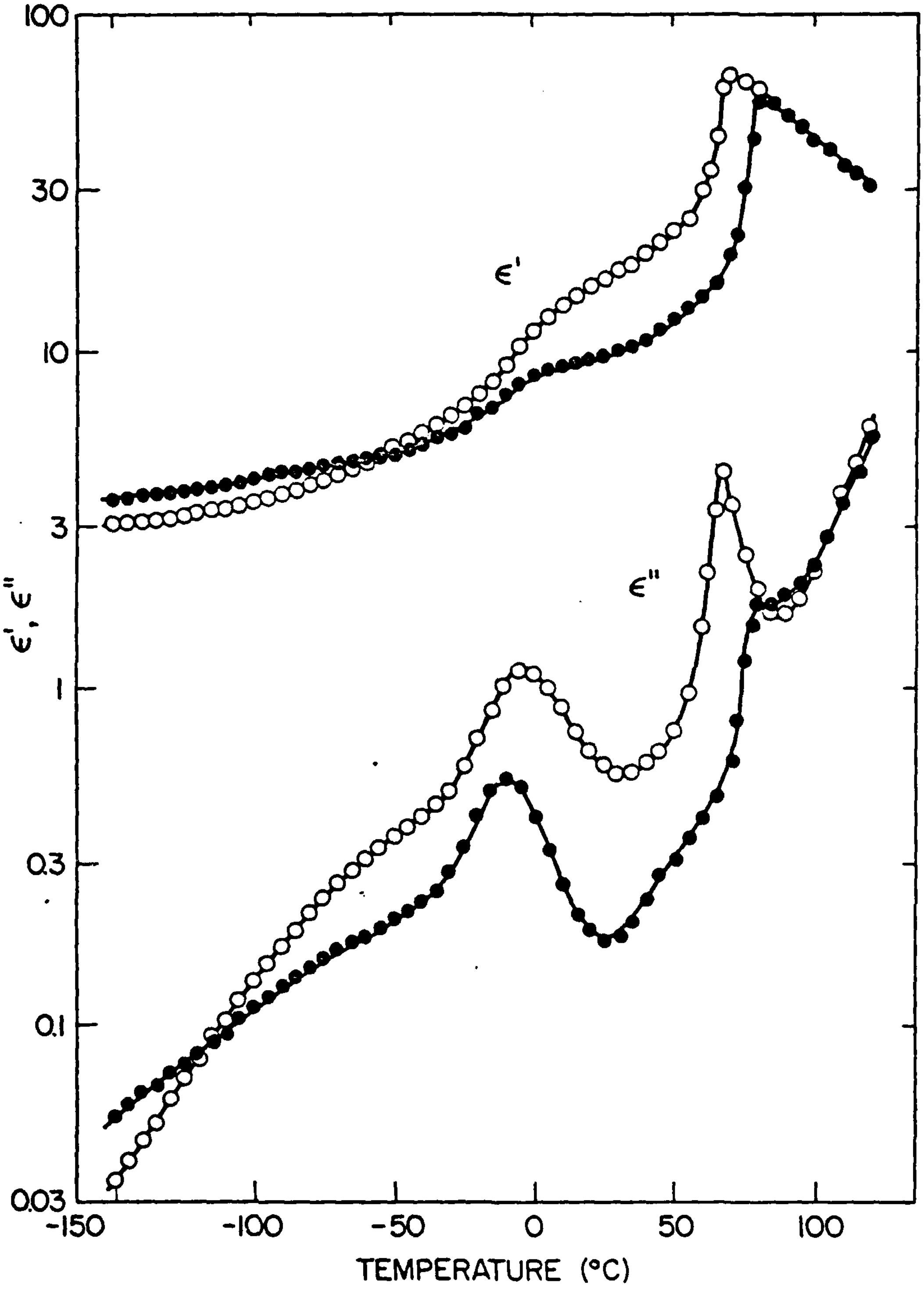
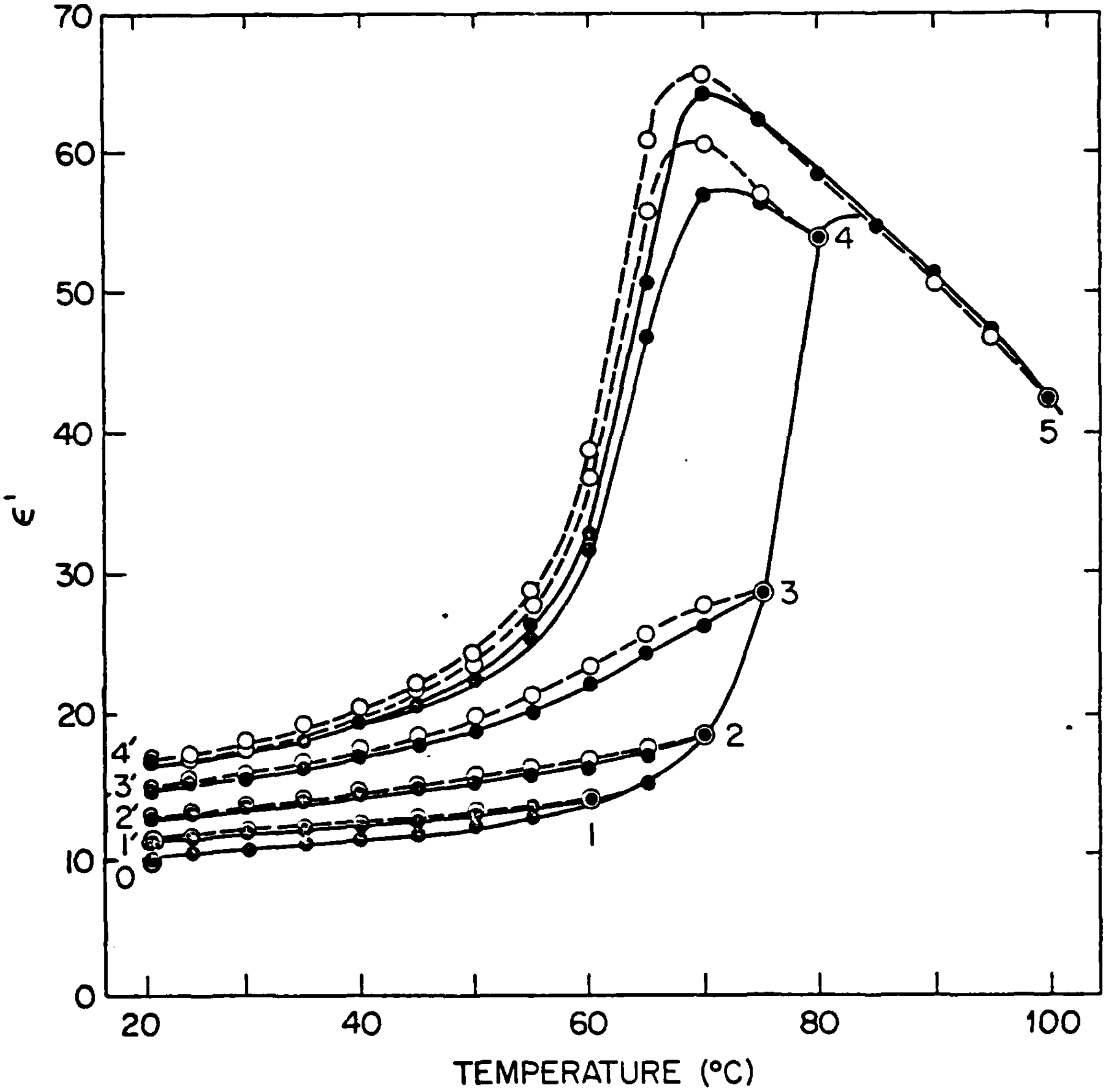


FIGURE 1



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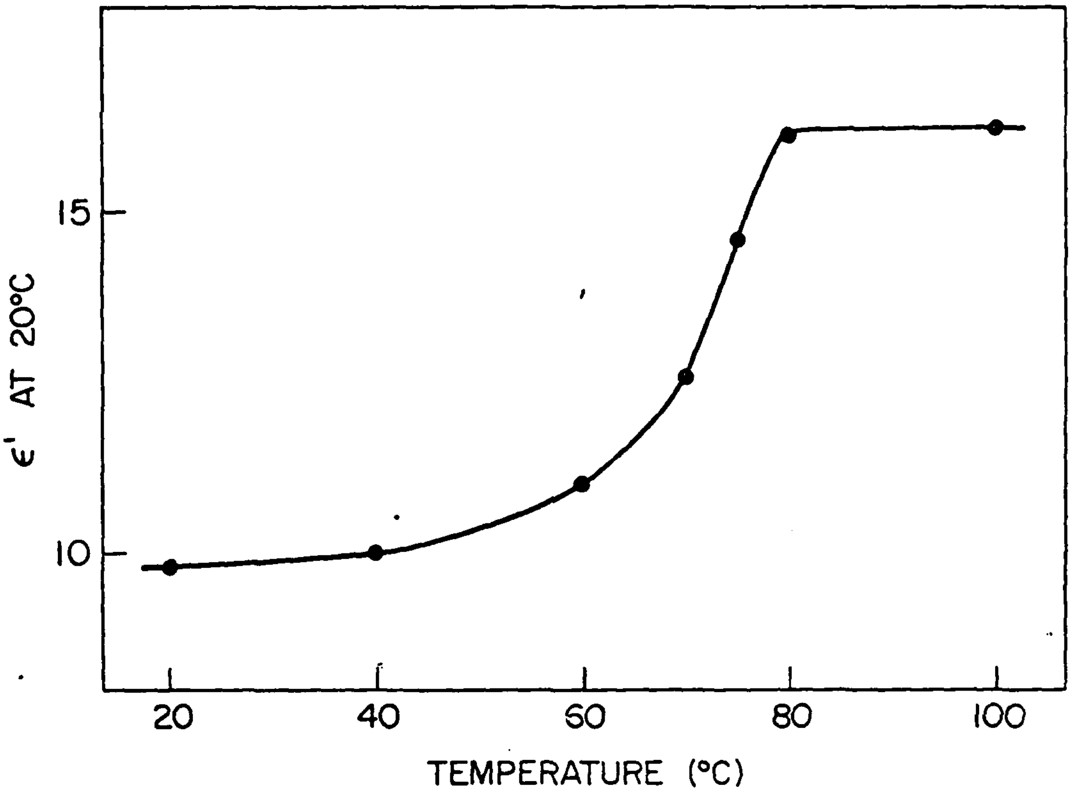
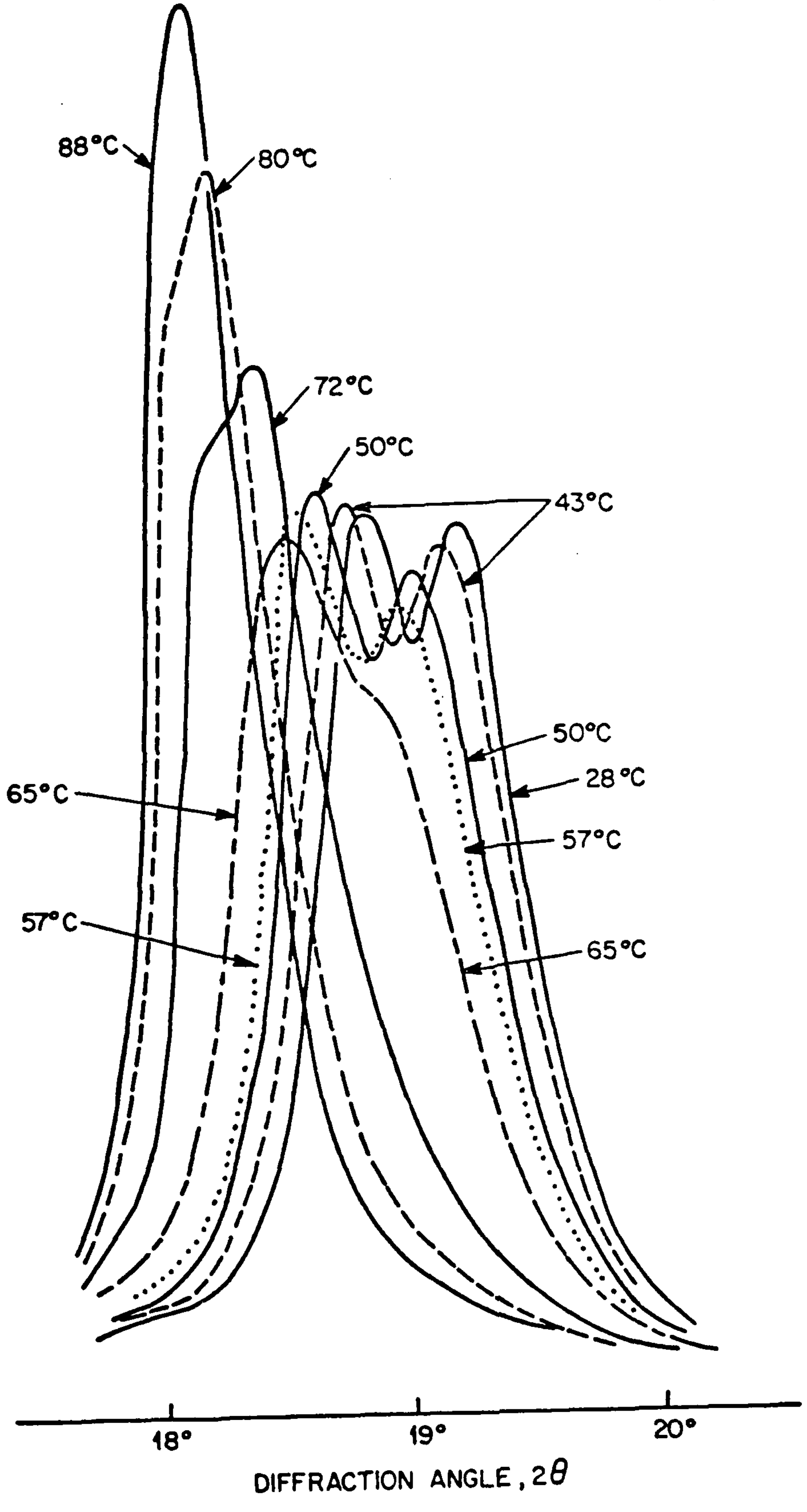


FIGURE 3

FIGURE 4


88°C
80°C
72°C
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43°C
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65°C
57°C
57°C
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20°
DIFFRACTION ANGLE, 2θ

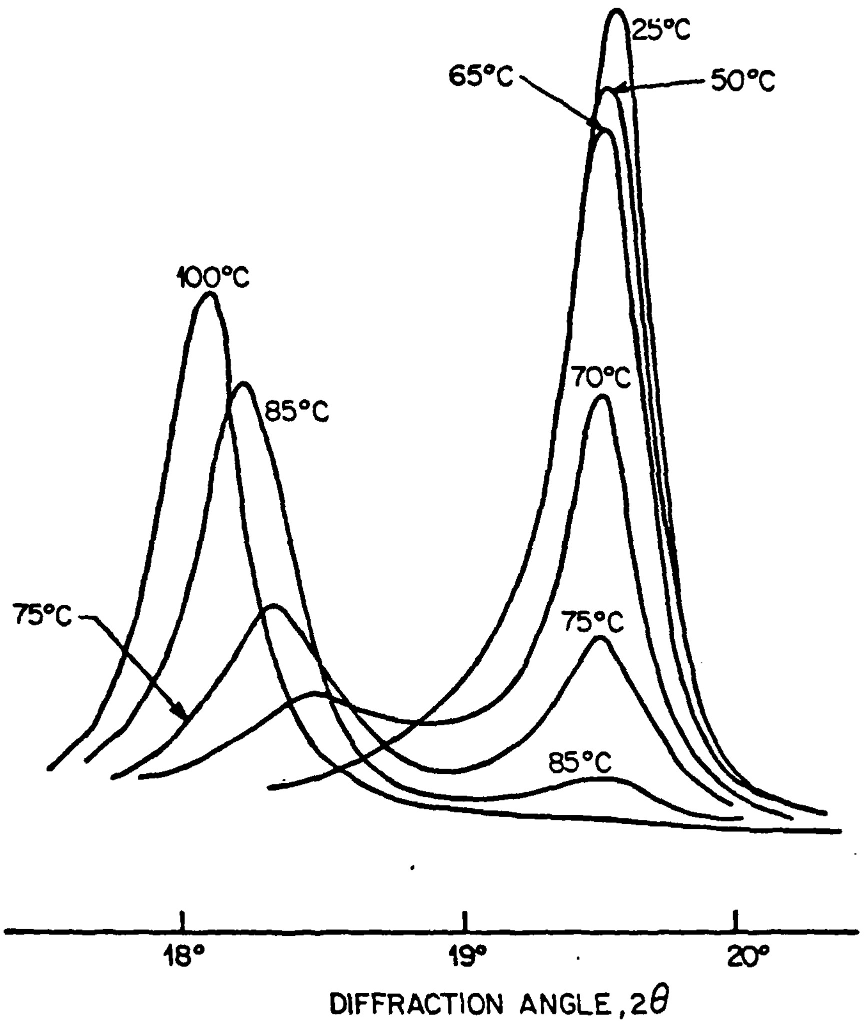
25°C
50°C
65°C
100°C
85°C
70°C
75°C
75°C
85°C
18°
19°
20°
DIFFRACTION ANGLE, 2θ

FIGURE 5

[illegible]

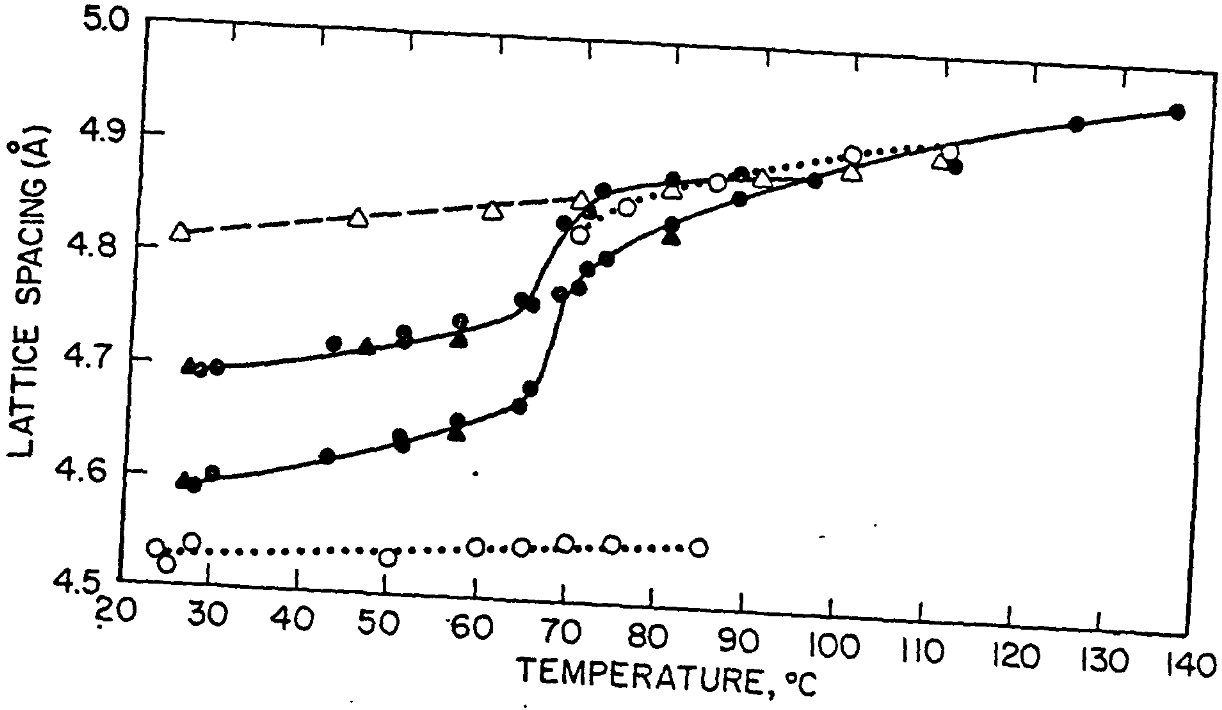
5.0
4.9
4.8
4.7
4.6
4.5
LATTICE SPACING (Å)
20
30
40
50
60
70
80
90
100
110
120
130
140
TEMPERATURE, °C

FIGURE 6

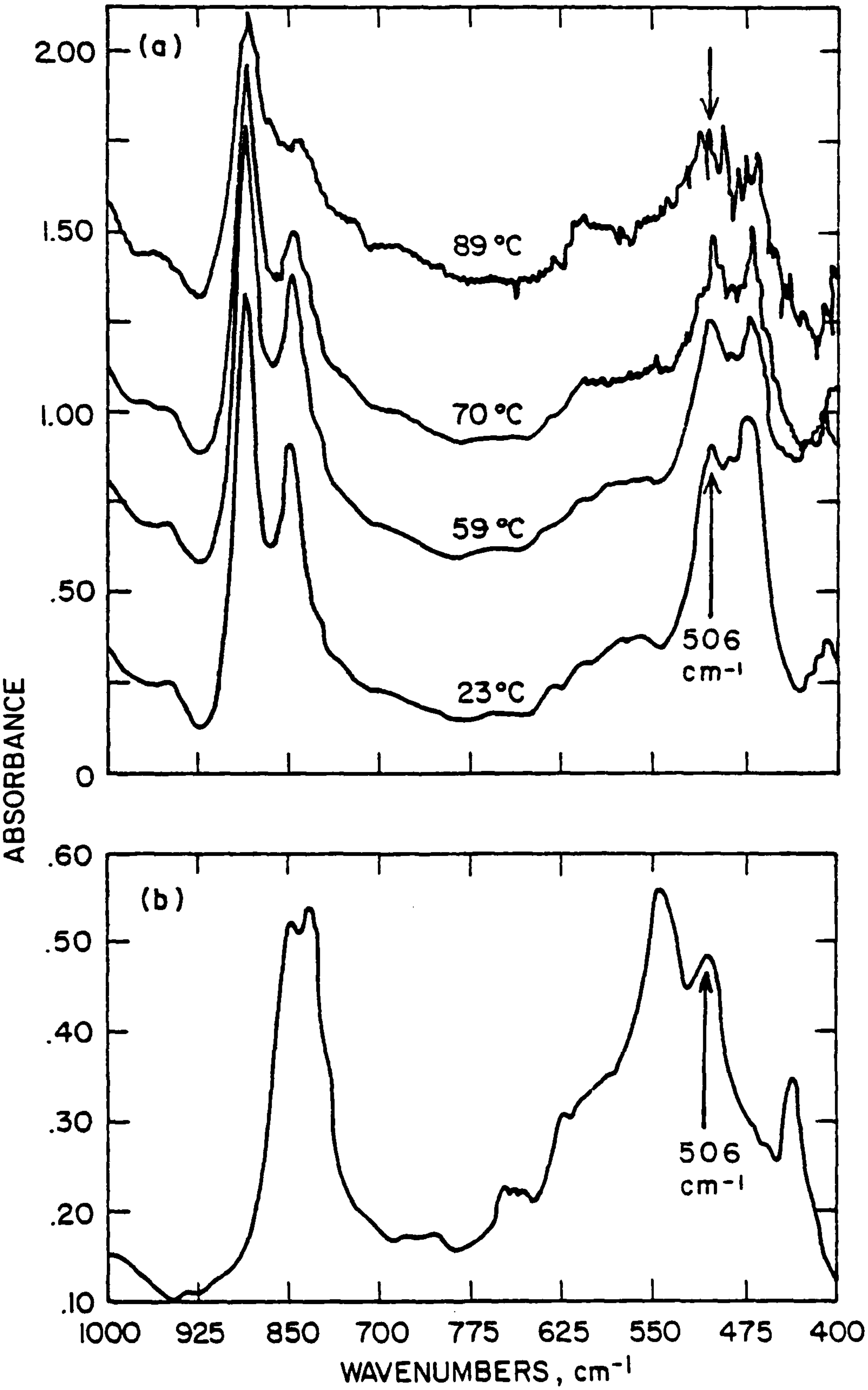
(a)
2.00
1.50
1.00
.50
0
89 °C
70 °C
59 °C
23 °C
506
cm-1
ABSORBANCE
(b)
.60
.50
.40
.30
.20
.10
506
cm-1
1000
925
850
700
775
625
550
475
400
WAVENUMBERS, cm-1

FIGURE 7

SP472-3/35

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