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Mechanical Properties of Polythylene Terephthalate under Selected Conditions and Methods of Preparation

by

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Part I

CALORIMETRIC STUDIES OF DRAWN POLYETHYLENE TEREPHTHALATE

by

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Introduction

A new approach to the study of drawn polymers is calorimetry[1]. The proposed procedure for studying a polymer by calorimetry is to measure the heats of fusion and heats of crystallization of samples drawn different amounts and at different temperatures. The dependence of these heats upon draw, along with other data, should provide some insight into the changes that occur during drawing.

The purpose of this report will be to determine the effects of draw ratio and draw temperature upon the heats of transition of PET. These values will be measured with the dynamic micro-calorimeter. Crystallinity will be evaluated through density measurements and orientation by x-ray diffraction patterns.

The results of these measurements will be used in an attempt to deduce the mechanism by which PET crystallizes and orients upon drawing. These results will also be correlated with the previous results obtained by infrared[2] and morphological studies[3].

Thermal Parameters for Undrawn PET

As a control for the drawn samples, a sample of the glassy PET was cut to a weight sufficient to give optimum results in the calorimeter. A second order transition, an exotherm and an endothermic peak appeared between the starting temperature (18°C) and final temperatures (280°C). The baseline was very smooth and had a consistent positive slope.

The exotherm identified as a cold crystallization peak, began at 108°C. The difference in temperature steadily increased and reached its maximum value at 129°C. The baseline after the peak was of slightly less slope than before, but remained positive. The best baseline appeared to be a straight line drawn between temperatures of 108°C and 147°C. The slope of this extrapolated baseline was the same as before the peak. The area of this peak was 1.27 ± 0.02 in^2. Considering the calibration constant of 70.1 ± 1.2 mcal/°C-min at 122°C, the heat of crystallization is found to be 1.05 ± 0.04 kcal/mole of repeat unit.

The endotherm began at 227°C and reached its minimum value at 259°C. There was no evidence of any shoulder on the peak. A baseline could be drawn between 227° and 275°C with its slope equal to the baseline before the peak. Because of the temperature range this peak may be assigned to the melting of crystalline regions of the sample[4]. The temperature of the minimum of the peak is 260°C $\pm$ 1.5°C. Since the weight is known and the area of the peak can be measured, a heat of fusion was calculated. With a calibration constant of

77.96 ± 1.33 mcal/°C-min at 232°C the heat of fusion is found to be 1.55 ± 0.04 kcal/mole of repeat unit. It should be noted that this value of the heat fusion is for an annealed sample since the polymer crystallized (below 150°C) and from that temperature until the melting point at 227°C, it was annealing. This was indicated previously through the density measurements.

Thermal Parameters for Drawn PET

Strips of amorphous PET were clamped in the jaws of the Instron TT-C and drawn at 0.1 inches/minute. The temperatures of draw was adjusted to 60°C or 85°C. The polymer sample was stamped with parallel lines and after drawing the spacings were measured to give a per cent draw. The draw ranged from 75% to 300 ± 10%. The portion of the sample drawn 75% was in an unnecked but slightly drawn region. Portions of sample, drawn more than 75% were from the well formed necking region in samples drawn at both temperatures.

A feature of this thermogram of samples from >160% at 60 and 85°C is the lack of a cold crystallization exotherm from ambient to 150°C. There is no trace of such a peak near 120°C where cold crystallization occurred in the undrawn sample. This was the case for all samples drawn over approximately 150%.

There is a definite endotherm similar to the endotherm in the undrawn sample. It begins at approximately 228°C and reaches a minimum value at 259°C. The peak returns to a constant baseline at 273°C. There is, however,

a shoulder on the low temperature side of the peak (257°C) that was not observed in the undrawn sample.

The thermogram of the samples drawn less than 160% at 60° and 85°C showed a cold crystallization exotherm at approximately 160°C and a maximum value at 129°C. The melting endotherm began at 226°C and had a peak at 260°C, similar to the undrawn sample. However, there is a slight trace of a shoulder at 259°C.

The heats of fusion of various samples of PET, as a function of the amount of draw, are fitted to a straight line with none of the points deviating more than 25%. Assuming a linear relationship, the data are expressed by the following formula:

$$\Delta H_f(\text{kcal/mole}) = 1.53 + 1.10 \times 10^{-3} D \qquad (60^\circ C \text{ and } 85^\circ C)$$

where D is the per cent draw.

The temperature of the minimums on the melting and endotherm were experimentally the same with a value of 259° ± 1.5°C.

The crystallinity of each sample was calculated from the density. The crystallinity does not increase above the value of an undrawn sample until the polymer has been drawn more than 160%. Thus strain-induced crystallization at 60°C and 85°C does not occur until the sample has been drawn more than 160% or until a neck has formed.

The samples were annealed in the calorimeter to 225°C at 10°C/min and the resulting crystallinities determined Crystallinity increased upon

annealing to 50%; crystalline content is a linearly increasing function of draw although the slope is very small ($1.55 \times 10^{-2} \frac{\%X}{\%D}$).

Some of the drawn samples were examined by x-ray diffraction to determine the crystallinity and the nature of the orientation. The samples drawn less than 160% were found to be unoriented and amorphous to x-ray diffraction. After annealing, these samples were crystalline but were still unoriented. However, samples drawn above 160% were semicrystalline and oriented. Upon annealing, the crystallinity increased and the orientation was perfected. These results agree with the relative crystallinities of the samples determined by density measurements.

To this point, samples have been studied that were drawn below or very near the glass transition temperature. The following set of data concern samples drawn well above the glass transition temperatures where chain mobility is greatly increased. The samples were drawn at 2 and 5 inches/minute with the sample temperature at 105°C and 114°C. Although the sample narrowed somewhat between the jaws of the Instron, there was no well defined necking region as in previous experiments. The per cent draw ranged from 78 to 360%. At a draw temperature of 105°C and 114°C, all samples produced similar thermograms. The thermogram is very similar to that for an undrawn polymer (and to samples drawn less than 160% at 60° and 85°C). The cold crystallization exotherm starts at 108°C, reaches a maximum at 127°C and returns to the baseline at 145°C. The baseline, after the peak, has a less positive slope than before the peak as in previous cases. The extrapolated baseline is drawn

between 107° and 145°C. A heat of crystallization of 1.16 kcal/mole is found. The baseline, after the exotherm, is linear and with a slight positive slope until 224°C where melting begins. The minimum value is reached at 260°C. The baseline before and after the fusion endotherm are of identical slope and, therefore, it is easy to extrapolate a straight baseline across the peak. It is not necessary, in this case to use two fixed points in order to establish the desired baseline. The heats of fusion as a function of draw ratio at 105°C and 114°C were fitted with a smooth curved line instead of a straight lines. It is, however, possible to approximate the curve by two straight lines. The formula for these lines are:

$$D<250\% \quad \Delta H_f(\text{kcal/mole}) = 1.55 + 2.00 \times 10^{-4} D \quad (105^\circ\text{C and } 114^\circ\text{C})$$

$$D>250\% \quad \Delta H_f(\text{kcal/mole}) = 1.22 + 1.53 \times 10^{-4} D \quad (105^\circ\text{C and } 114^\circ\text{C})$$

The slope for D greater than 250% is close to that of samples drawn at lower temperatures. The average peak temperature was 260° ± 1.5°C. The heat of crystallization as a function of the amount of draw are fitted by an assumed straight line with no point deviating more than 4%. The slope is positive by small $(2.8 \times 10^{-4} \frac{\text{kcal/mole}}{\%D})$.

Unannealed drawn samples did not increase in crystallinity as measured by density; in other words all samples had approximately 3% crystalline content. Upon annealing, all samples increased in crystallinity to the same level -- 40%.

Flat plate x-ray patterns confirmed the results of density measurements. All samples, no matter how much they were drawn at 105°C, appeared completely amorphous. Annealed samples were crystalline but there was no

orientation (diffraction patterns appeared as rings and not spots).

The heats of crystallization for samples drawn at 114°C as a function of draw are unusual in that the slope of the line is negative. The points show greater scatter deviating as much as 5%.

Densities were measured and crystallinities calculated. For unannealed samples there is a slight, linear increase in crystallinity with draw in contrast to results at 105°C. Crystallinity of annealed samples also increased linearly with draw with no point deviating more than 2%.

Flat-plate patterns confirmed the crystallinity data. Unannealed, drawn samples showed a very slight amount of crystallinity and orientation upon annealing. Crystalline content increased greatly upon annealing but orientation was slight.

An important fact must be kept in mind when considering samples drawn at low temperatures (60° and 85°C). This fact is the low mobility for whole molecules and for aggregates of molecules such as the ball-like structures. When a sample is drawn at a low temperature, the strain may not be relieved by slipping of molecules past one another; the primary means to relieve the strain will be uncoiling of segments of molecules in the amorphous or tie-molecule regions of the sample. This rearrangement can only relieve the major portion of the strain. Previous results indicate this mechanism of elongation occurs up to approximately 160% draw. After this draw ratio has been reached, the ball-like areas must change in order to relieve strain. Therefore, above 160% draw,

the strain will be "experienced" by the balls themselves; to relieve the strain, the molecules in these regions will uncoil and if in proper registry will crystallize.

No crystallization will occur below 160% draw because there is uncoiling and elongation in tie molecule regions. Above 160% draw, the chains in the ball-like regions uncoil to relieve the strain. The more strain imposed on the molecules the more uncoiling and subsequent crystallization[5]. The relationship between strain and crystallinity is nearly linear.

Since there is no measurable difference between strain induced crystals and heat induced crystals, all samples are nearly identical at the melting point whether they have been initially drawn enough to strain crystallize or not. The linear increase in the heat of fusion with draw is a result of greater trans content in the crystalline regions. As molecules were put under strain the gauche isomers are converted to trans isomer, and the more trans isomer the easier it is for the sample to crystallize.

The results relating to samples drawn at 105° and 114°C can be interpreted in a similar manner. The most important difference is that the higher temperatures give greater mobility to the molecular chains. The strain imposed on the sample drawn at higher temperatures is relieved by rearrangement of the amorphous molecules. This is similar to drawing at lower temperatures except that the molecules in this case move more easily past one another and therefore may not uncoil as much. However, the more the

sample is drawn the more tie molecules that will be drawn taut; and these tie molecules will transfer the strain to the ball-like regions in which they are incorporated.

In the ball-like regions the chains are also more mobile and, instead of relieving strain by conversion from gauche to trans isomers, the strain is partially relieved by movement of molecules past one another in the draw direction. The fact that less conversion to trans isomers is found in samples drawn at 105°C than at 85°C has been verified by infrared studies[2]. Thus there may be an increase in alignment of the chains upon drawing but, since there is little uncoiling (gauche isomers converting to trans amorphous isomers), there is little crystallization. Molecules that are incorporated in more than one ball-like structure may uncoil but there are not enough of these to produce a notable change in crystallinity. Thus annealed and unannealed densities do not depend on the amount of draw at higher temperatures.

Conclusions

The results that have been discussed are consistent with the following conclusions:

1. As a sample is drawn at lower temperatures (60° and 85°C) the strain imposed on it is relieved by uncoiling and some alignment of molecules; at temperatures over 100°C strain is relieved by the molecules sliding past one another in the draw direction.

2. Strain induced crystallization will only occur in a PET sample when it is drawn more than 160% at temperatures near the glass transition.

3. Heat-induced crystals and strain-induced crystals have similar heats of fusion.

4. When a sample is drawn and annealed under strain, the molecules further uncoil by an amount proportional to the stress in order to relieve the strain.

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Part II

MORPHOLOGICAL RESEARCH

by

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Morphological research during the subject period has been proceeding in two areas:

1. Attempts to better visualize the modular structure of PETP and to determine the original and reproduce variations in the module size in order to determine their effect on mechanical properties.

2. Extension of the morphological research on PETP to polycarbonate.

In this report we will describe briefly some of the interesting results obtained by A. Siegman in his work with Polycarbonate (PC). The work of J. Klement of PETP is progressing satisfactorily, but is at such a stage that little new and definite can be added to that previously reported. PC was chosen as a second polymer for these studies because it, also, is ductile below its Tg (ca. 145°C) and can be quenched to the glass and crystallized subsequently by thermal treatments. Its physical properties are strongly affected by annealing treatments below Tg (80-110°C) and by orientation. Previous work (Carr, Geil, Baer, J. Macromol. Sci. (Phys.) in press) has shown that it has a modular structure in the glassy state, whose size, in contrast to our past scouting work on PETP, is affected by thermal treatments.

Annealing of solvent case (methylene chloride) amorphous thin films at Tg results in significant crystallization, crystallization which proceeds in a way unique in polymer crystallization to date. Following an initial aggregation to form patches of the modules, similar to those observed in PETP, actual, well formed lamellar, simple crystals of PC develop up to several microns in size with the lamellar oriented parallel to the substrate. Following this individual arms of lamellar grow out from the center of the crystal with the lamellar oriented normal to the substrate. A spherulitic structure develops which gradually fills in and becomes finer in texture. There is a suggestion that the polymer in the simple crystals recrystallizes (at Tg) during formation of the spherulites at higher temperatures (160°C) a somewhat similar crystallization process is followed, except that the structures formed are more irregular than those formed at 145°. In one sample large spherulites were also found to form during annealing at 110°C, 35° below Tg. The latter results are being examined further, the more usual result being only changes in module size.

All of the above results indicate an extremely high degree of molecular mobility in the PC samples. One obvious possibility leading to such mobility would be retention of solvent in the films, the solvent acting as a plasticizer. Gas chromatography indicates that 3% methylene chloride (chosen because its boiling point is near room temperature) is retained in a <1000 A thick film after air drying for 12 hours and 1% after drying at 110°C for 1 hour. Films used for the studies mentioned above were dried to a greater extent than this, but probably still retained some solvent. Although this amount of retained

solvent would be expected to reduce Tg, the results obtained are still beyond that expected. Present research is directed toward (a) measuring amount of retained solvent after vacuum drying, (b) using melt quenched films which should be solvent free, (c) examining the effect of annealing dry films in the 80-145° range, particularly in the 80-110°C range where substantial changes in physical properties are known to occur.

Part III

CRYOGENIC RELAXATION BEHAVIOR

by

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The aim of this part of the research effort was to study the effect of molecular organization in poly(ethylene terephthalate) (PET) on its mechanical properties at cryogenic temperatures, using dynamic mechanical methods as the primary research tool. Accordingly a torsional pendulum, capable of measuring low levels of internal friction at temperatures down to $4^{o}K$ was designed and constructed in 1966. Preliminary data on the cryogenic relaxation behavior of quenched, annealed, drawn and heat set films of poly(ethylene terephthalate) were reported by Kuriyama and Baer[1], and by Armeniades et al[2]. These data showed the occurrence of relaxation maxima, which were significantly affected by orientation and crystallinity.

A large part of the research effort during 1967 was devoted towards optimizing the operation of the torsional pendulum and improving the accuracy of its measurements. The preliminary data reported in (1) and (2) contained several errors. These were due to contamination of the helium atmosphere in the torsional pendulum with condensing air during low temperature operation and to the use of specimen geometries unsuitable for measurement of low shear

forces. These and several other sources of error have been eliminated by modifying the pendulum design, and changing the specimen geometry and experimental procedure. The accuracy of the measurements obtained with the current instrumentation and experimental technique has been verified by reproducing Sinnott's data on atactic polystyrene[3] using thin film specimens. Our results are shown in Figure 1 and are in complete agreement with Sinnott. In other experiments the torsional pendulum was used for internal friction measurements on a Nb-Mo alloy which was also tested with a resonant bar apparatus at higher frequencies. The data, plotted on Figure 2, are in complete agreement with the resonant bar measurements (see Figure 3) and furthermore demonstrate the ability of the cryogenic torsional pendulum to detect levels of damping as low as 10^{-4}. These results of the polystyrene and Nb-Mo alloy experiments enable us now to treat current pendulum data with considerable confidence of their reliability.

Recent internal friction measurements on quenched, annealed, drawn and heat set poly(ethylene terephthalate) films are shown in Figures 4, 5, and 6. As previously noted the β maximum in logarithmic decrement, decreases with increasing crystallinity and splits into two peaks in the oriented and heat set specimens. However, significant changes in relaxation behavior due to molecular organization also occur below 80°K. Figure 7 shows a linear plot of the logarithmic decrement of various PET specimens in this temperature range. Comparison of amorphous PET with samples 1a and 1b drawn uniaxially below their T_G, shows an increase in the intensity of the δ peak with orientation. These two samples were not annealed and their crystallinity is

due to drawing only. Nondrawn annealed samples 2a and 2b show a relaxation maximum (ϵ) at about 20°K, which increases with crystallinity. As expected, drawn and heat set samples show both the δ and ϵ relaxation peaks, the δ peak being most pronounced in the uniaxially drawn specimen. Our hypothesis at present is that the δ peak may result from chain alignment due to drawing, whereas the ϵ peak may be associated with motions in the crystalline region. Specific investigations aimed at gaining some insight on the molecular origin of the cryogenic relaxation peaks are currently under way. Considerable difficulties in resolving these peaks and measuring their activation energies are caused by the proximity of the broad and much more intense β peak, which is presumably associated with motions of the carboxylene and methylene groups[4]. For this reason experiments at higher frequencies are not planned at present. We are, however, in the process of examining the relaxation behavior of related polymers such as polycarbonate, poly(phenylene oxide) and poly(phenylene sulfide). Comparison of these polymers may shed some light on the role of in-chain phenyls on the cryogenic relaxations.

The molecular orientation in drawn specimens, which show the pronounced relaxation maximum at 48°K will be measured using well developed X-ray, polarized infrared and optical birefringence techniques.

Another approach involves use of low temperature infrared spectroscopy in an effort to correlate sharpening or shifting of the various absorption bands with molecular relaxations[5]. This method may be of considerable value in correlating crystallinity and orientation on relaxation from a submolecular viewpoint since there are specific infrared bands in PET assigned to crystalline and folded molecular conformations[6].

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FIGURE CAPTIONS

Figure 1: Shear modulus and logarithmic decrement of atactic polystyrene as a function of temperature.

Figure 2: Internal friction measurements of NB-1.3% Mo using the cryogenic torsional pendulum.

Figure 3: Arrhenius plot of loss peaks in NB-1.0% Mo measured at different frequencies.

Figure 4: Shear modulus and logarithmic decrement of noncrystalline PET as a function of temperature. (O) amorphous Mylar film; (Δ) PET quenched from the melt in ice water.

Figure 5: Shear modulus and logarithmic decrement of nonoriented PET at different crystallinities as a function of temperature ———, amorphous Mylar film; -----, annealed from the glass 10 hours at 110°C (38% crystalline); — — — —, crystallized from the melt by slow cooling (56% crystalline).

Figure 6: Shear modulus and logarithmic decrement of three crystalline PET samples with different orientation ———, melt-crystallized nonoriented (56% crystalline); -----, uniaxially drawn 600%; heat-set 30 min. at 200°C (51% crystalline); — — — —, Mylar A sequentially biaxially drawn and heat-set, 54% crystalline).

Figure 7: Cryogenic relaxation behavior of seven PET specimens with different molecular organization.

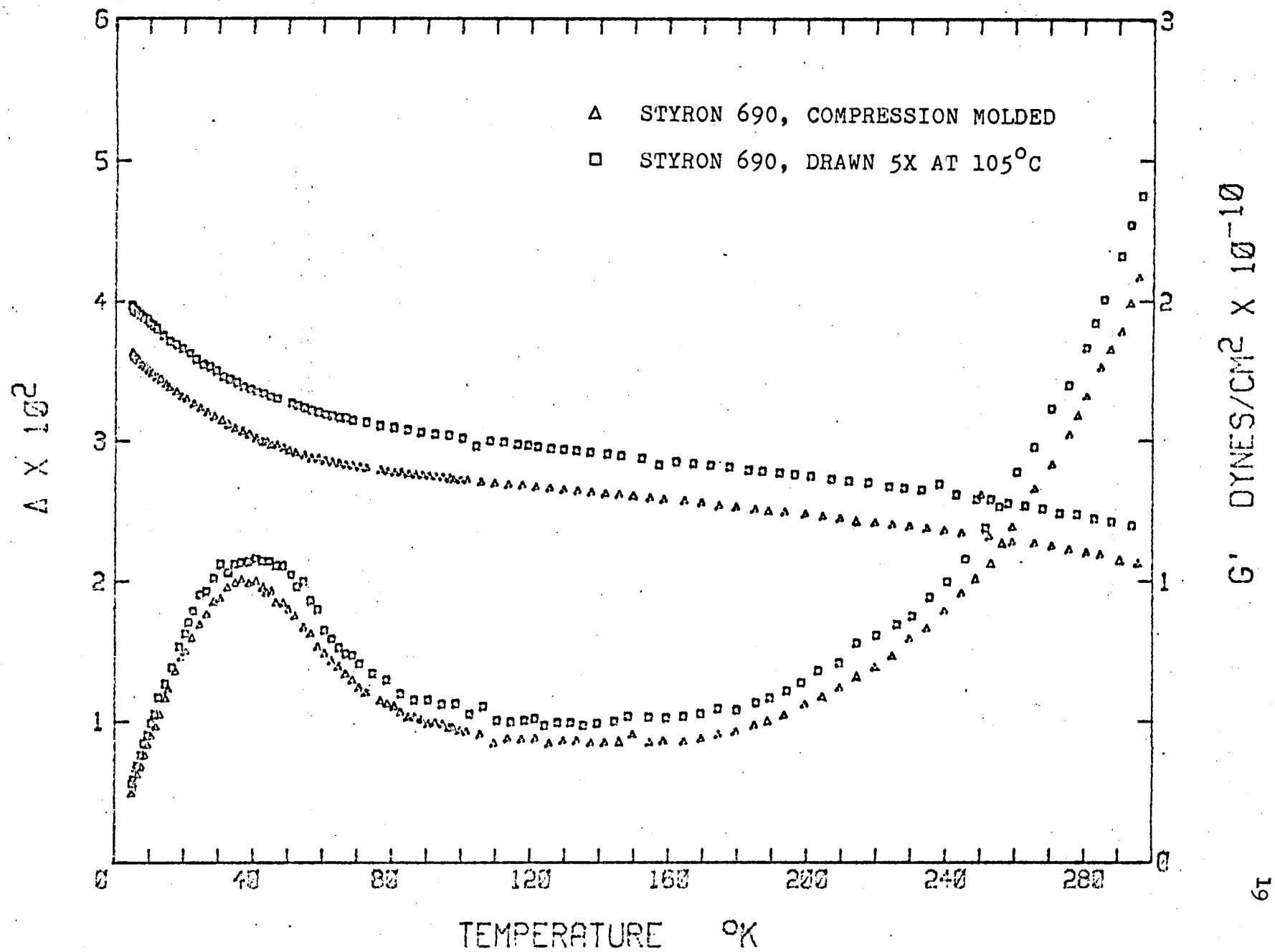
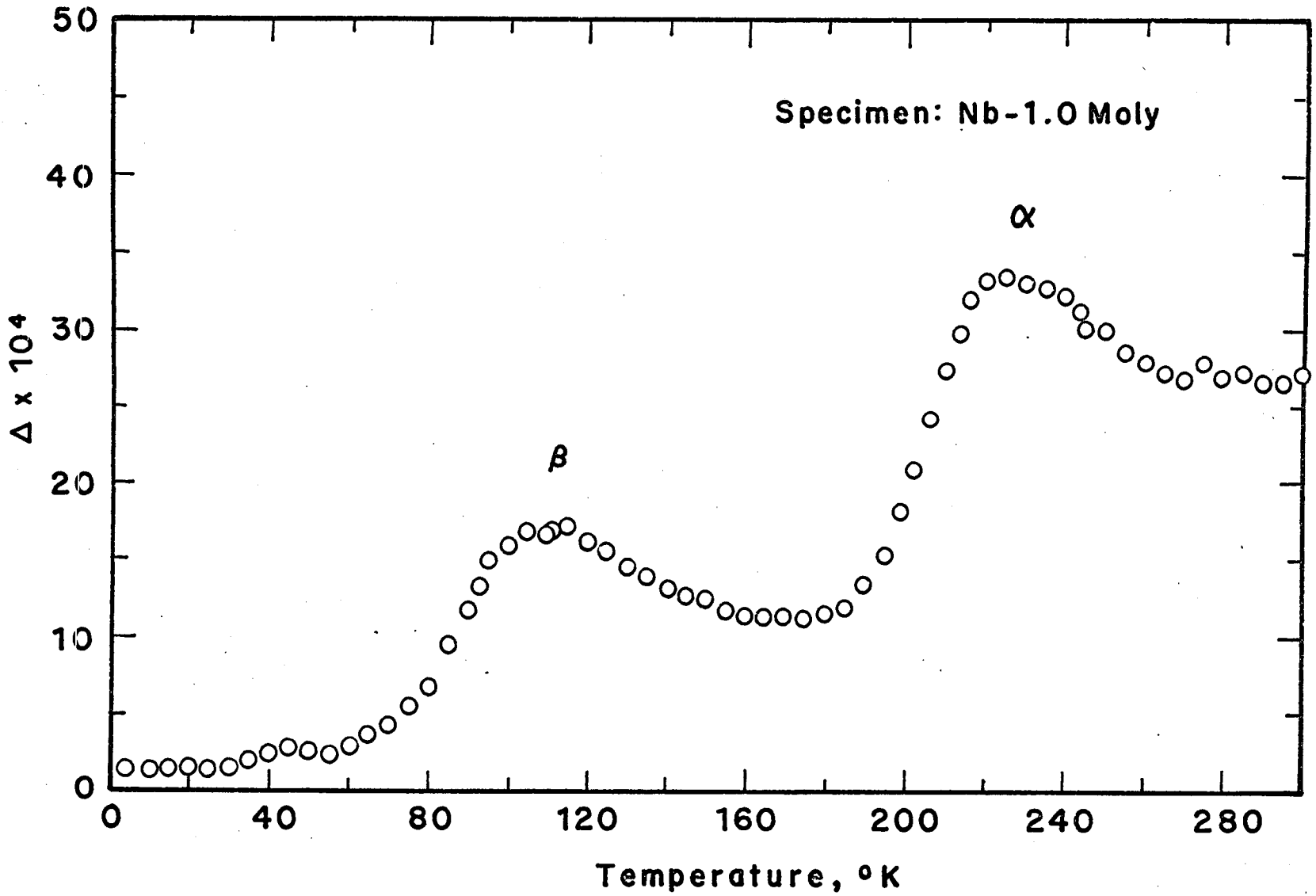

STYRON 690, COMPRESSION MOLDED
STYRON 690, DRAWN 5X AT 105°C
Δ X 10²
G' DYNES/CM² X 10⁻¹⁰
TEMPERATURE °K
0
40
80
120
160
200
240
280
1
2
3
4
5
6

Figure 1


Specimen: Nb-1.0 Moly
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β
Δ x 10⁴
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30
40
50
0
40
80
120
160
200
240
280
Temperature, °K

Figure 2

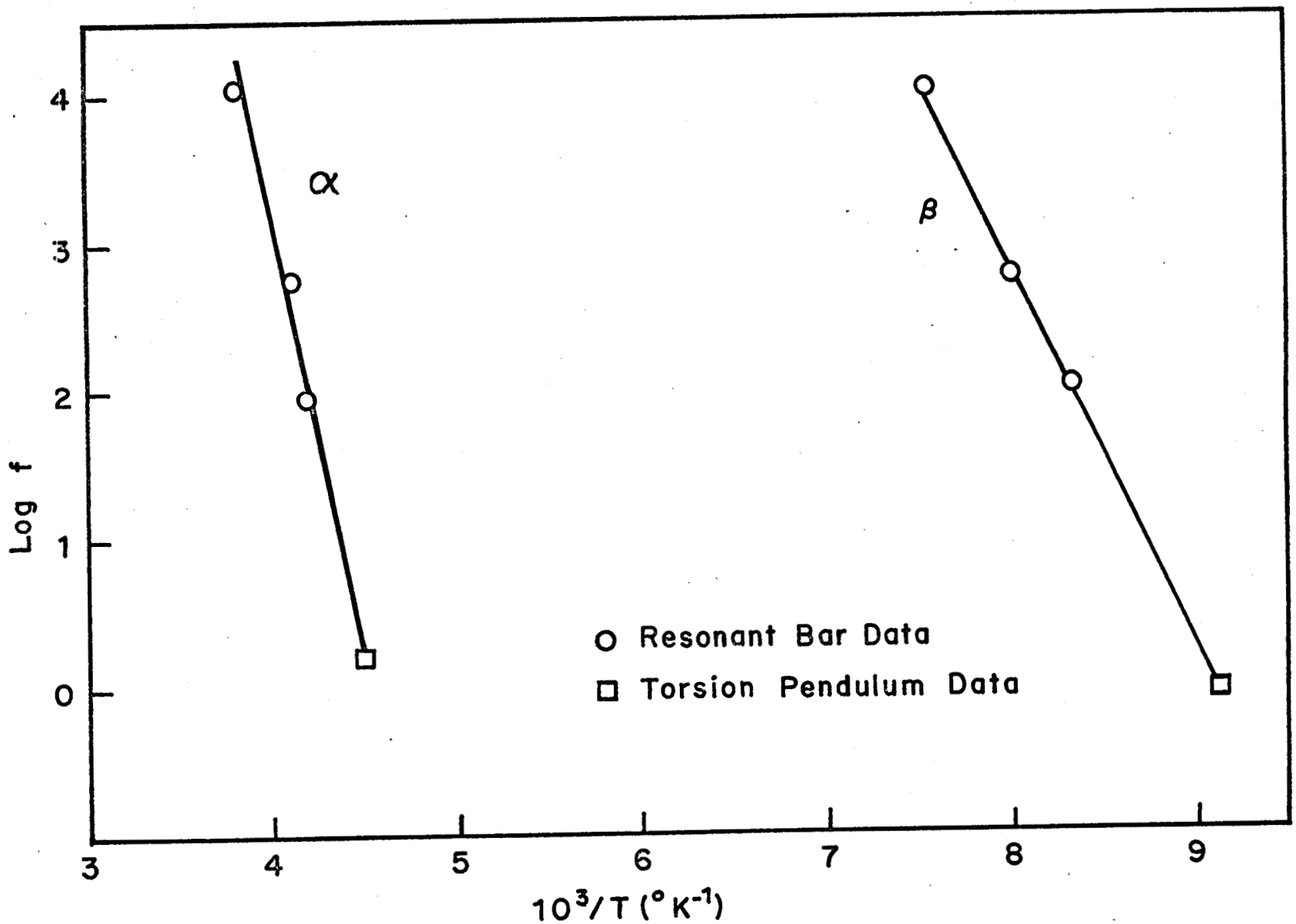
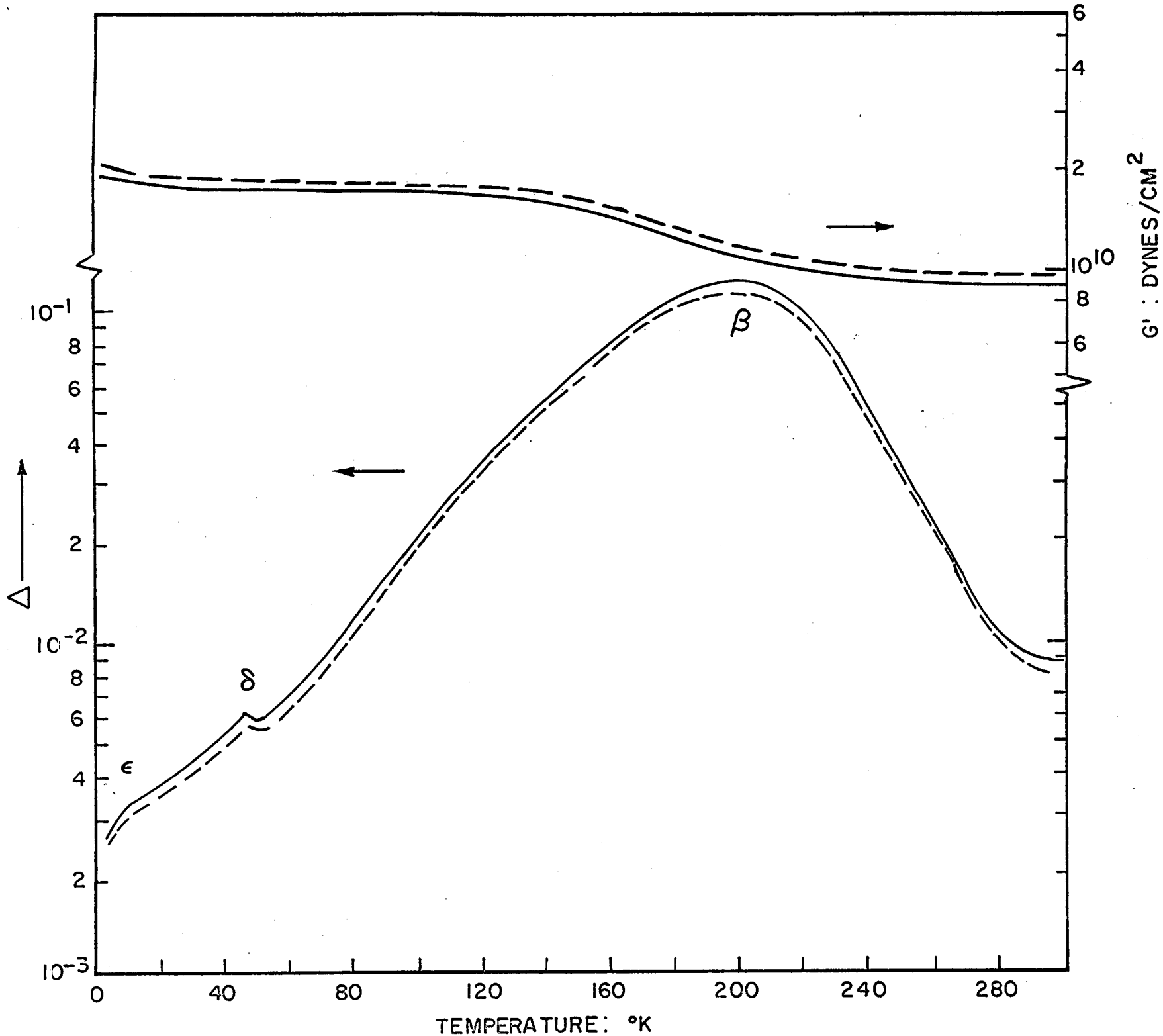

Log f
4
3
2
1
0
α
β
Resonant Bar Data
Torsion Pendulum Data
3
4
5
6
7
8
9
10³/T (°K⁻¹)

Figure 3


6
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G' : DYNES/CM^2
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8
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10^{-2}
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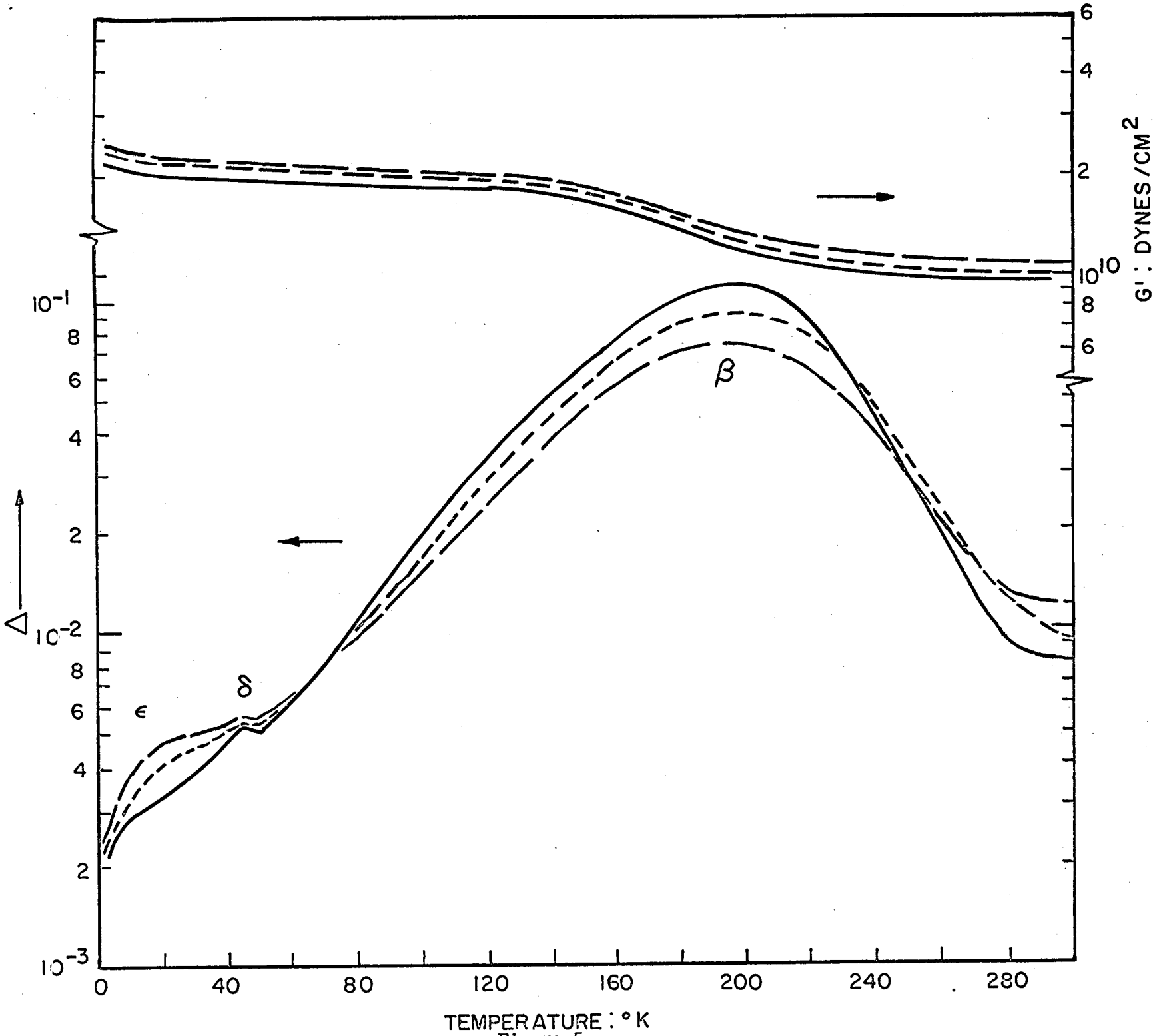
TEMPERATURE: °K

Figure 4


G' : DYNES/CM^2
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TEMPERATURE : °K

Figure 5

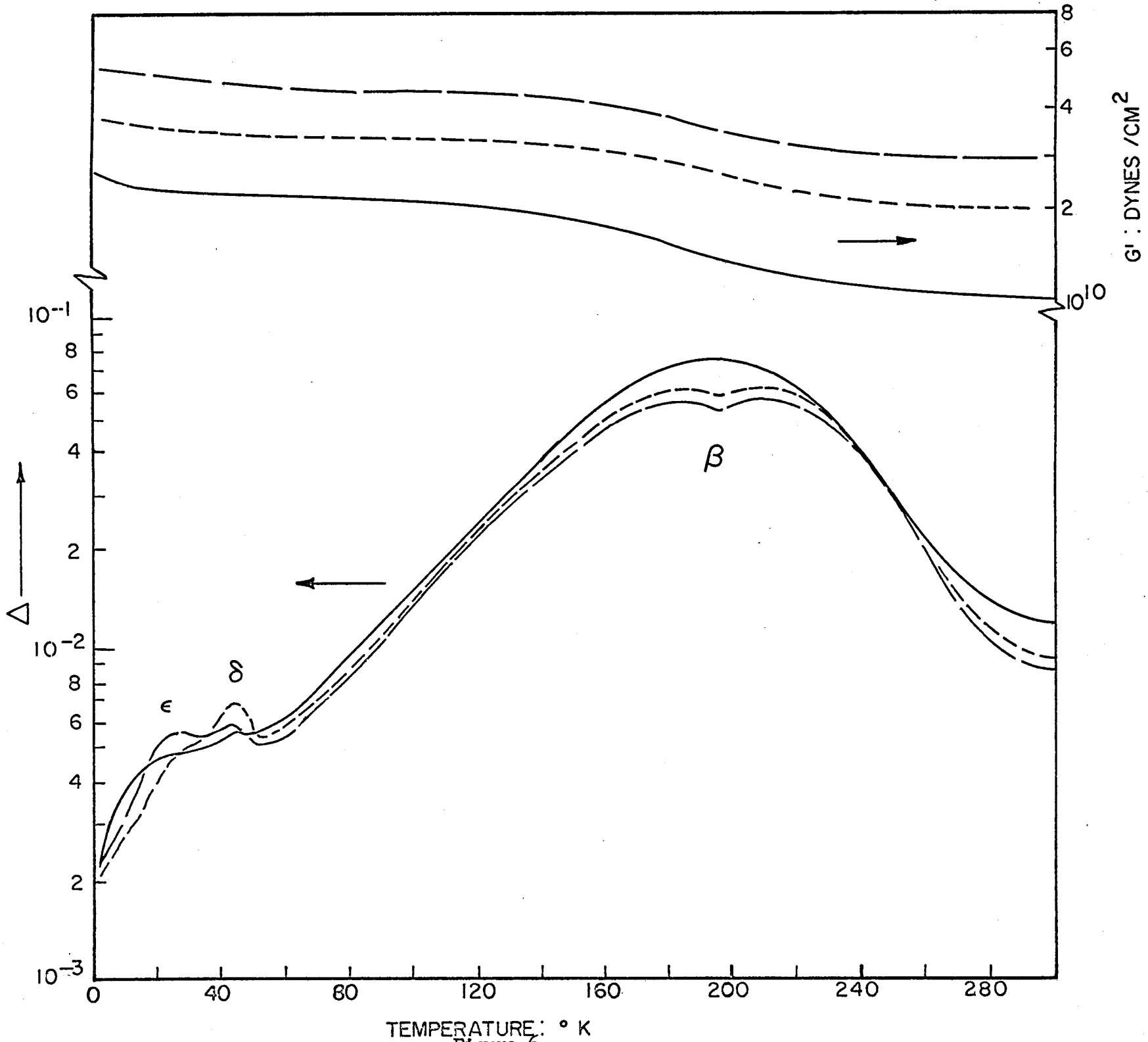
G' : DYNES /CM^2
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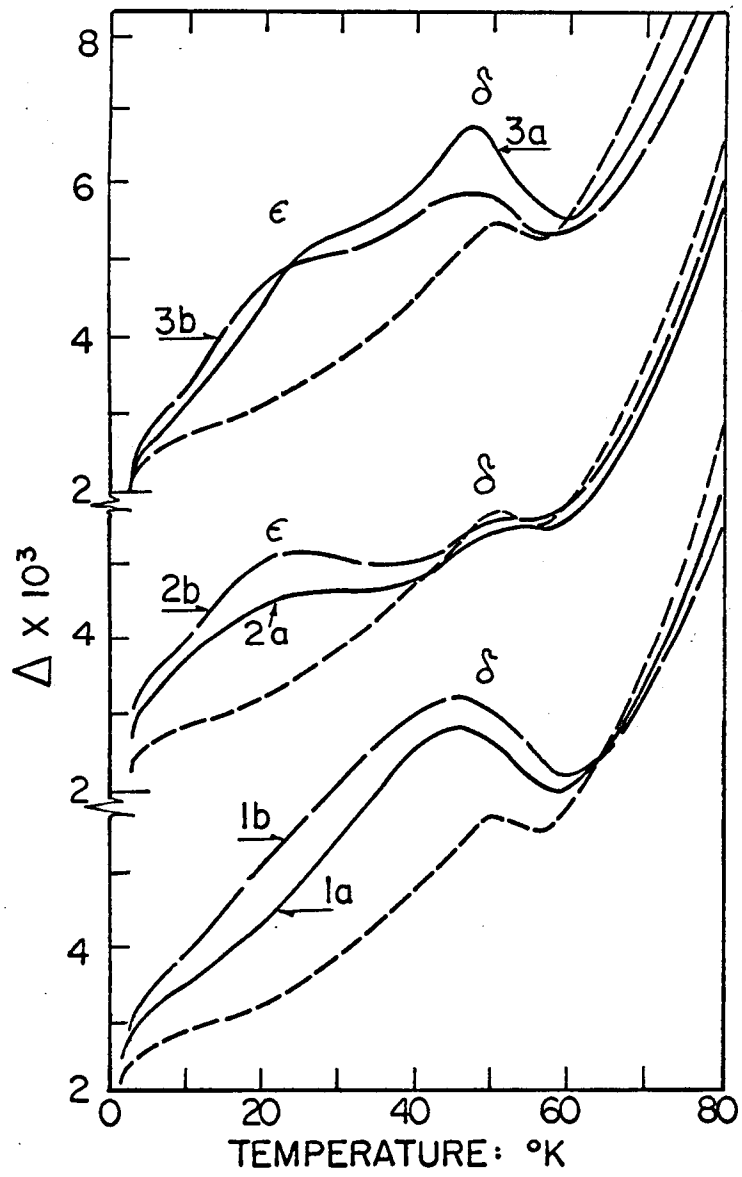
Figure 6



--- Amorphous PET

1a Uniaxially Drawn 4X at 45 C, 16% Crystalline

1b Uniaxially Drawn 5.5X at 65 C, 28% Crystalline

2a Annealed 3 hrs at 100 C 32% Crystalline

2b Annealed 1 hr at 180 C 64% Crystalline

3a Uniaxially Drawn 5.5X 65 C, Heat Set at 200 C for 1 hr, 55% Crystalline

3b Biaxially Oriented 3X3 and Heat Set, 55% Crystalline

Figure 7