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ELECTRICAL RELAXATION IN PURE AND ALKALI
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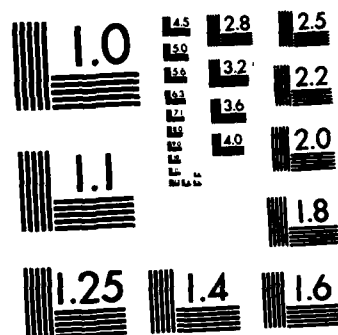
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ELECTRICAL RELAXATION IN PURE AND ALKALI METAL-
THIOCYANATE COMPLEXED POLY(ETHYLENE OXIDE)

by

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ELECTRICAL RELAXATION IN PURE AND ALKALI METAL-
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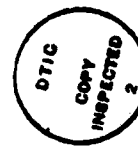
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ABSTRACT

Audio frequency complex admittance and DSC studies have been performed on pure poly(ethylene oxide)(PEO) and PEO complexed with alkali metal thiocyanates over the temperature range 5.5-380K. The dielectric constant of the complexed materials is found to be greater than for pure PEO. A discontinuity in the conductivity is found which increases in temperature as the size of the cation increases. In every case, the discontinuity is associated with a feature in the DSC results. Next, some evidence is given that water may enhance the formation of amorphous complexed PEO. In pure PEO, α and γ relaxations are observed in good agreement with previous work. A thermal anomaly is found corresponding to γ . In addition, α is identified in pure PEO. Very little difference is found for the γ relaxation between pure PEO and PEO-LiSCN and PEO-NaSCN. For PEO-KSCN, three distinct peaks are found in the γ relaxation region. These results are consistent with a γ transition interpretation for γ where the cations reside within the helical channels at low temperatures. $\leftarrow$

5-5MMA

ALPHA SUB A

ALPHA SUB C

1. INTRODUCTION

Ion conducting poly(ethylene oxide) (PEO) has been attracting a great deal of attention because of possible applications as a solid state electrolyte (1-18). As electrical relaxation has proved a useful technique in the study of polymers, such studies of PEO complexed with various thiocyanates were undertaken and the results are presented in the present work.

2. EXPERIMENT

Audio frequency measurements of the capacitance, C , and the conductance, G , divided by the frequency, were performed using a fully automated, microprocessor controlled bridge constructed by one of the authors (C.G.A.). The bridge balances the sample against a known capacitance and resistance in parallel. It operates at the five frequencies given by $\log(f) = 2, 2.5, 3, 3.5$ and 4 with f in Hz. The bridge is at least as sensitive and accurate as the best commercially available manual bridge.

The measurements were performed in a Cryogenics Associates temperature controlled dewar with an eight sample holder. The eight sample holder allows essentially simultaneous measurement of eight different specimens, thus allowing a useful comparison of materials. The data were taken with the temperature held constant with approximately one hour allowed for equilibration at high temperatures decreasing to about 20 minutes at the lowest temperatures. Above 45K the temperature is measured using a Rosemount Eng. Co. platinum resistance thermometer and below 45K it is measured using a CryoCal Inc. germanium resistance thermometer. The temperature is controlled using a 27 Hz feedback temperature controller and in general was controlled to within 0.001K. The absolute temperature is probably accurate only to about 0.1K. Other results obtained using this system are given elsewhere (19-24).

Films of PEO (Polysciences, MW 5×10^6) complexed with various salts were obtained by preparing solutions of the materials and casting the liquid on a teflon plate. The films were degassed and air dried. All operations were performed at room temperature though the dissolution of the salts was usually performed

at about 70C. The proportion of polymer repeat unit to salt was 4.5 to 1 for NaSCN and KSCN and 5 to 1 for LiSCN. The films were finally vacuum dried at 60C for about 24 hours. In addition, the samples are actually dried a second time under vacuum in situ since all measurements are performed under vacuum and initially the temperature is increased to about 100C. This procedure takes place over about 10 hours. In some cases acetonitrile was used as the solvent, but in general, methanol proved to be more effective.

The samples were disks ranging from 0.25 to 1 mm thick and about 1.5 cm in diameter. Aluminum electrodes were evaporated onto the surfaces. While one electrode covered one full surface, the other electrode was only about 0.9 cm in diameter for convenience of loading into the sample holder, which was originally designed for other purposes.

This procedure limits the accuracy of the complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, or the conductivity, σ , since the usual equations:

$$C = \frac{\epsilon_0 \epsilon' A}{d} \quad (1)$$

or

$$G = \frac{\sigma A}{d} \quad (2)$$

are not strictly applicable because of the geometry. ϵ_0 is the permittivity of free space and A and d would be the area and thickness of a perfect parallel plate specimen. However, since absolute conductivities are not the primary subject of the present paper, eqs. (1) and (2) were applied anyway using the average area of the two faces for A. Further, no thermal expansion correction factor was included because of an apparent lack of literature values for PEO. The geometrical factor, A/d, was only measured at room temperature and ϵ' at 300K and 1000 Hz calculated from eq. (1). The values of ϵ' at all other frequencies and temperatures were calculated assuming that ϵ' varies as the capacitance. The values of ϵ'' were then calculated from:

$$\epsilon'' = \frac{\epsilon' G}{\omega C} \quad (3)$$

and the conductivity was obtained from:

$$\sigma = \epsilon_0 \epsilon'' \omega. \quad (4)$$

These procedures place the absolute accuracy at about 10%. However, the relative uncertainty in ϵ' or σ is far better since both G/ ω and C are measured to about 1 aF for values up to 10 pF and to five significant figures above that.

Differential scanning calorimeter (DSC) measurements were carried out using a Perkin Elmer DSC-1B instrument. The measurements were performed over the temperature range 190-450K at a rate of 10C per minute. The instrument has a 15C maximum temperature error over the range studied.

3. RESULTS AND DISCUSSION

The results for ϵ' and ϵ'' or σ at three frequencies are shown in figs. (1)-(4) along with the significant portions of the DSC traces for the pure and complexed materials. For clarity, the electrical data are shown for decreasing temperatures only and the lines connect the datum points. To show a typical distribution of datum points, one complete set of 1000 Hz results are plotted in fig. (5).

In general, the low temperature values of ϵ' for the complexed materials are found to be higher than for pure PEO. The difference is attributed primarily to the polarization of the "ionic sublattice" at low temperatures.

The results for the high temperature conductivity plotted in figs. (2d), (3d), and (4d) show varying amounts of dispersion. The apparent lower conductivity for lower frequencies and high temperatures is attributed to blocking electrode effects. However, in all cases, there is very little difference (usually less than 1%) between values of σ at $10^{3.5}$ and 10^4 Hz and thus the values at 10^4 Hz well represent the conductivity of the samples. Further evidence for this assertion is given in figs. (3d) and (4d) where the results of Wright (2) are plotted in addition to the results of the present work. The agreement is quite good considering the uncertainty in the data and other possible variations such as sample preparation technique or water content.

3.1. Pure PEO

The results for a methanol based pure PEO sample are shown in fig. (1). The results for acetonitrile based films are identical. Several features are apparent. First, the α_a and γ

relaxations, which have been observed by other workers (25-34), are seen in fig. (1c). The notation is chosen to be consistent with books on the subject (25,26), however, several other workers use different nomenclatures (28,30-34).

The α_a relaxation is associated with the glass transition. This is confirmed by the DSC results shown in fig. (1c). The γ relaxation is ascribed to small scale motion of the main chains, and has been variously attributed to a "crankshaft mechanism" (35,36), "3-bond" or "4-bond" motions (37,38), "chain end hydroxyl groups" (26), or the " $tg^+t \rightleftharpoons tg^-t$ " transition (33). A consistent interpretation of the present results can be made in terms of the latter mechanism.

A third relaxation is apparent in fig. (1d) which is superimposed on the DC conductivity. The peak position is close to a mechanical relaxation peak reported by Connor et al. (29) or Kalfoglou (39) and thus probably corresponds to the α_c relaxation which is associated with the crystalline phase.

Evident at higher temperatures still is the solid-liquid transition of the pure PEO. The DSC peak occurs at a higher temperature than the conductivity anomaly. A major contribution to this effect is that the conductivity data were taken by slowly decreasing temperature and the DSC data are for rapidly increasing temperatures. Thus, the hysteresis is not surprising. Further, the DSC peak is about 5-10°C higher than that reported by Kusy and Turner (40) for similar molecular weight samples. This is within the error of the present instrument but may imply that it is biased toward high temperatures, in this temperature range at least.

These features are to be compared with the following results for PEO complexed with various alkali metal thiocyanates.

3.2. PEO-AM(SCN)

The results for PEO complexed with some alkali metal thiocyanates are shown in figs. (2)-(5). The α_a relaxation which occurs at about 224K and 10,000 Hz in pure PEO is absent in all of the complexed materials. This is consistent with the present DSC measurements as no thermal anomalies are observed in the vicinity of 224K for any of the complexed samples.

This indicates that no amorphous, pure PEO exists in the complexed materials. The remaining possibilities are crystalline PEO and various forms of complexed PEO. The DSC results rule out the presence of pure crystalline PEO for PEO-LiSCN and PEO-KSCN as no thermal anomaly is found where pure PEO is expected to melt (about 350K). For PEO-NaSCN there is an endotherm in the region of 350K. This type of behavior has previously been observed by Lee and Wright (5) in PEO-NaSCN showing none of the x-ray patterns characteristic of pure PEO. Therefore, in the light of the results of Lee and Wright, and the results for our lithium and potassium complexed material prepared using the same procedures, it is concluded that this endotherm is not due to melting of pure PEO and that, in fact, all the samples are fully complexed.

As regards the nature of the transition in PEO-NaSCN and PEO-KSCN (endotherm at about 400K), Lee and Wright attribute it to disordering of the complexed material within the network of chains between the lamellae (their phase II). That these materials are highly crystalline and thus allow for interlamellae material is consistent with the observations of Papke et al. (10). It is noted that the dominant thermal features for PEO-NaSCN and PEO-KSCN occur at higher temperatures than the discontinuity in conductivity for each material. The temperature difference is due to the hysteresis effect and DSC calibration error discussed above for pure PEO.

In contrast, PEO-LiSCN shows a very strong glass transition which is observed at about 290K as can be seen from the DSC results of fig. (2d). In samples not heated above 340K (fig. (2d)), there is a corresponding anomaly in the conductivity. Samples taken to higher temperatures do not exhibit this feature and in addition, have a lower conductivity at all temperatures. Based on the nature of the thermal anomaly and the fact that the samples are rubbery at room temperature, it is concluded that our PEO-LiSCN is highly amorphous. It is suggested that the amorphous character of the lithium complexed material is due to the presence of water, since the LiSCN was initially hydrated and attempts to remove the water of hydration were only partially successful. This conclusion is consistent with the observations of Weston and Steele (41) who find that polymers complexed using "wet" solvents were amorphous while those made using "dry" solvents were more crystalline.

For the pure PEO, PEO-LiSCN, and PEO-NaSCN samples, the γ relaxation occurs at about 195K and 10,000 Hz and is similar in the three materials. The possibility that pure PEO is present in the complexed material has already been ruled out. Further, the intensity of the γ relaxation in the complexed materials is not diminished from that in pure PEO. Consequently, there appears to be no difference in the γ relaxation between pure PEO and PEO-LiSCN and PEO-NaSCN. These results must be reconciled

with the results of Parker et al. (4) who conclude from x-ray work that the chains in the complexed materials are contracted. In this regard, the ttg^+ttg^- structure of the complexed material due to Papke et al. (10) is relevant. In fact, both the " $tg^+t \rightleftharpoons tg^-t$ " and "chain end hydroxyl group" mechanisms would be expected to be relatively unaffected by a shortening of the chains. However, as shown below, only the former mechanism is consistent with the results for PEO-KSCN.

Parker et al. (4) also suggest that the structure of the complexed material is a double helix rather than two single chains. At first sight, it would appear that the results of the present work are inconsistent with a double helix as it might be expected that the $tg^+t \rightleftharpoons tg^-t$ transition and hence the γ relaxation should be affected more than is observed. However, as these considerations are only intuitive, the possibility of a double helix cannot be ruled out. This is particularly true since the considerations of Parker et al. (4) help explain the results for PEO-KSCN.

As seen in fig. (4c), three peaks are observed in PEO-KSCN in the region of the γ relaxation. Three peaks are observed in PEO-KSCN prepared with both methanol and acetonitrile thus ruling out solvent effects. The explanation for this is that the lithium and sodium ions fit easily within the helical tunnels while potassium, being larger, produces more severe local distortions in the polymer chain. The distortions in turn introduce an inequivalence between the potential wells or barriers associated with the γ relaxation. In fact, Parker et al. (4) have pointed out that "calculations show that lithium and sodium ions may be readily accommodated within the cavities but that potassium ions are barely accommodated and require that two of the C-C bonds adopt rotation angles within the trans domain." As the γ relaxation is associated with the C-O bond, just this difference may be responsible for the difference in the relaxation spectrum between PEO-KSCN and the other alkali metal thiocyanates. Further, the differences in the relaxation spectrum are probably correlated with the differences in the IR spectra for PEO-NaSCN and PEO-KSCN reported by Papke et al. (10).

Finally, the results for PEO-KSCN rule out the "chain end hydroxyl mechanism" for the γ relaxation since it is difficult to understand how the

cations could have such a significant effect on the chain ends for PEO-KSCN but not for PEO-LiSCN or PEO-NaSCN.

4. SUMMARY

In summary, then, several results have been obtained by a complex admittance and DSC study of pure PEO and PEO complexed with various alkali metal thiocyanates:

- (1) The dielectric constant of the complexed materials is found to be greater than that for pure PEO.
- (2) A discontinuity in the conductivity is found which decreases in temperature as the size of the cation decreases. Each discontinuity is correlated with a thermal anomaly.
- (3) PEO-LiSCN is amorphous at low temperatures while PEO-NaSCN and PEO-KSCN are highly crystalline. It is suggested that the amorphous phase is easier to form in the presence of water.
- (4) For PEO-LiSCN and PEO-NaSCN, the position of the γ relaxation is about the same as for pure PEO. For PEO-KSCN three relaxations are observed in the region of the γ relaxation. These results are consistent with a $tg^+t \rightleftharpoons tg-t$ relaxation of a helical structure where the cations reside within the helical channels at low temperatures.

ACKNOWLEDGMENTS

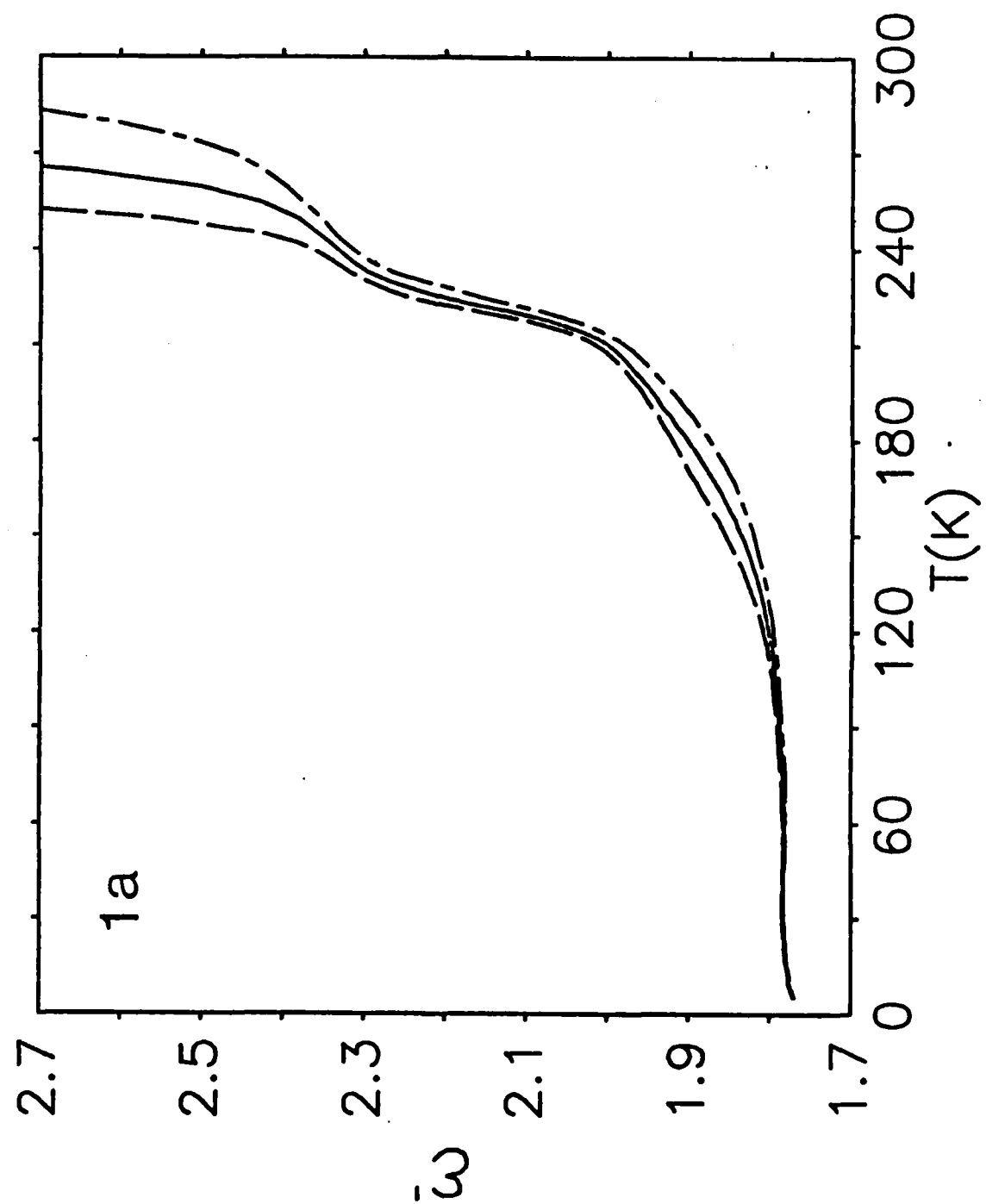
The authors would like to thank D.F. Shriver and R. Dupon of Northwestern University, A.V. Chadwick and M. Worboys of the University of Kent at Canterbury, U.K., and D.R. Figueroa of Simon Bolivar University, Caracas, Venezuela for many helpful discussions. This work was supported in part by the Office of Naval Research.

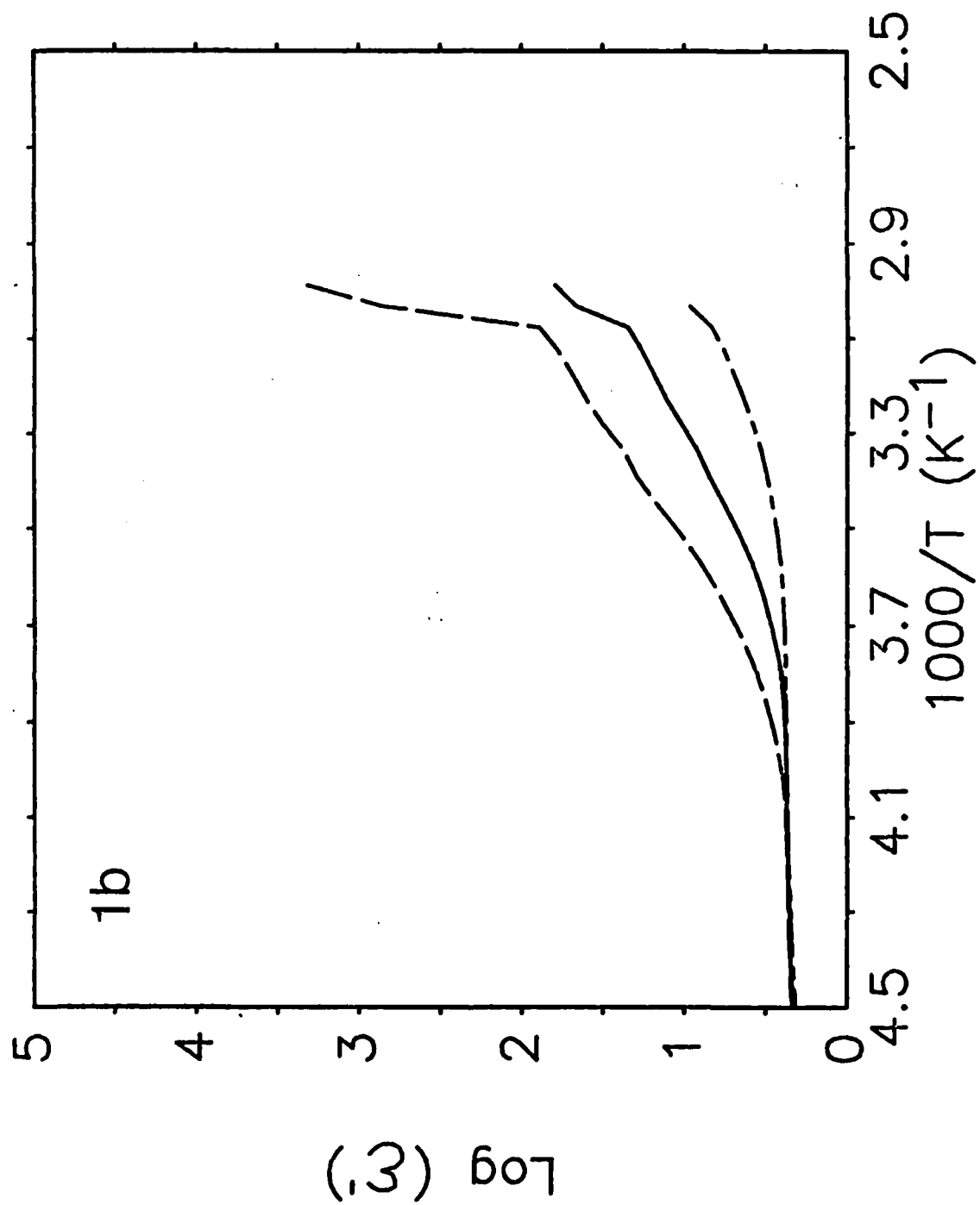
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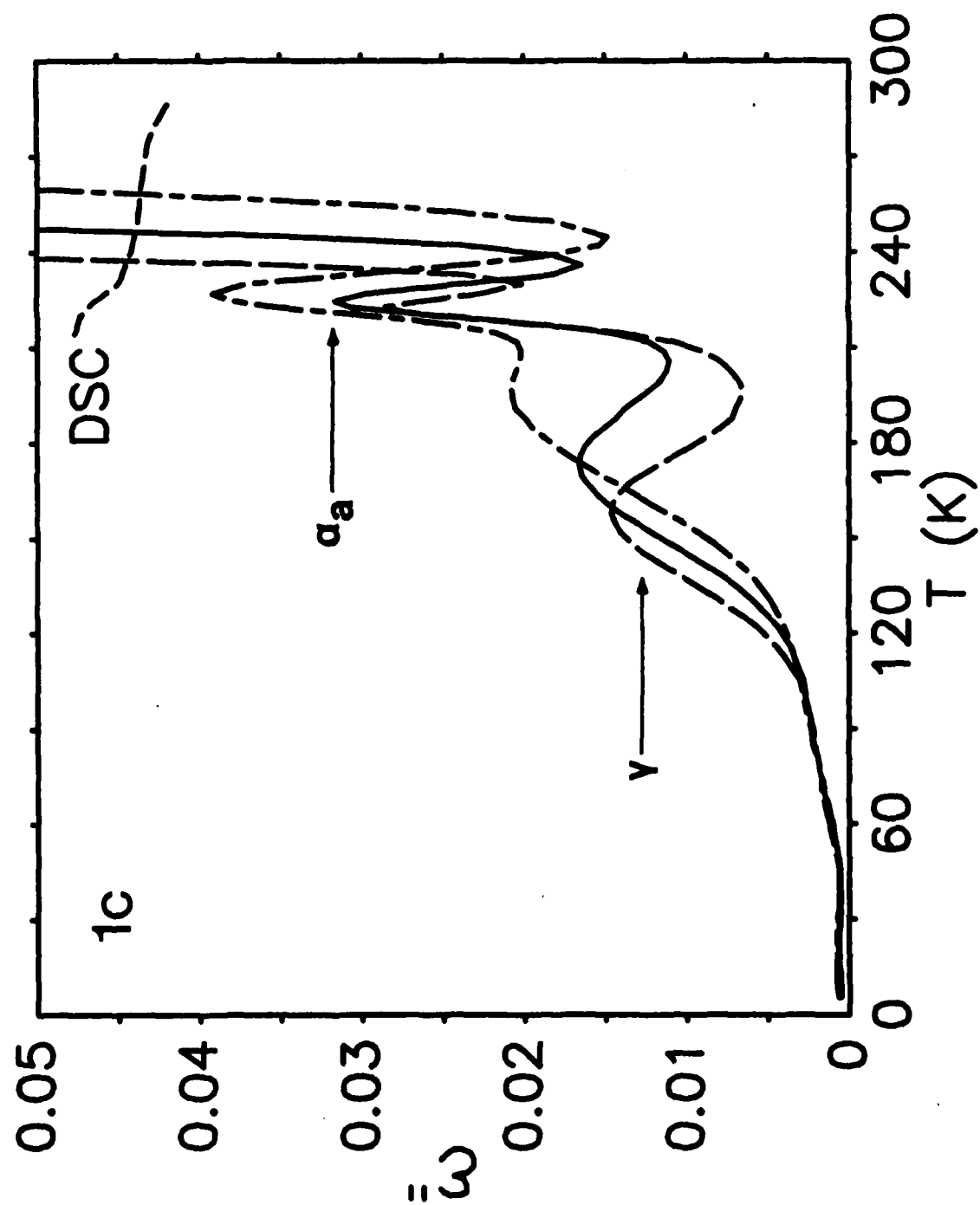
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Fig.1. Pure PEO. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz. The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. $T(K)$ (b) $\text{Log}(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. $T(K)$; DSC discontinuity height of 2 units (arbitrary) (d) $\text{Log}(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC peak height of 36 units.







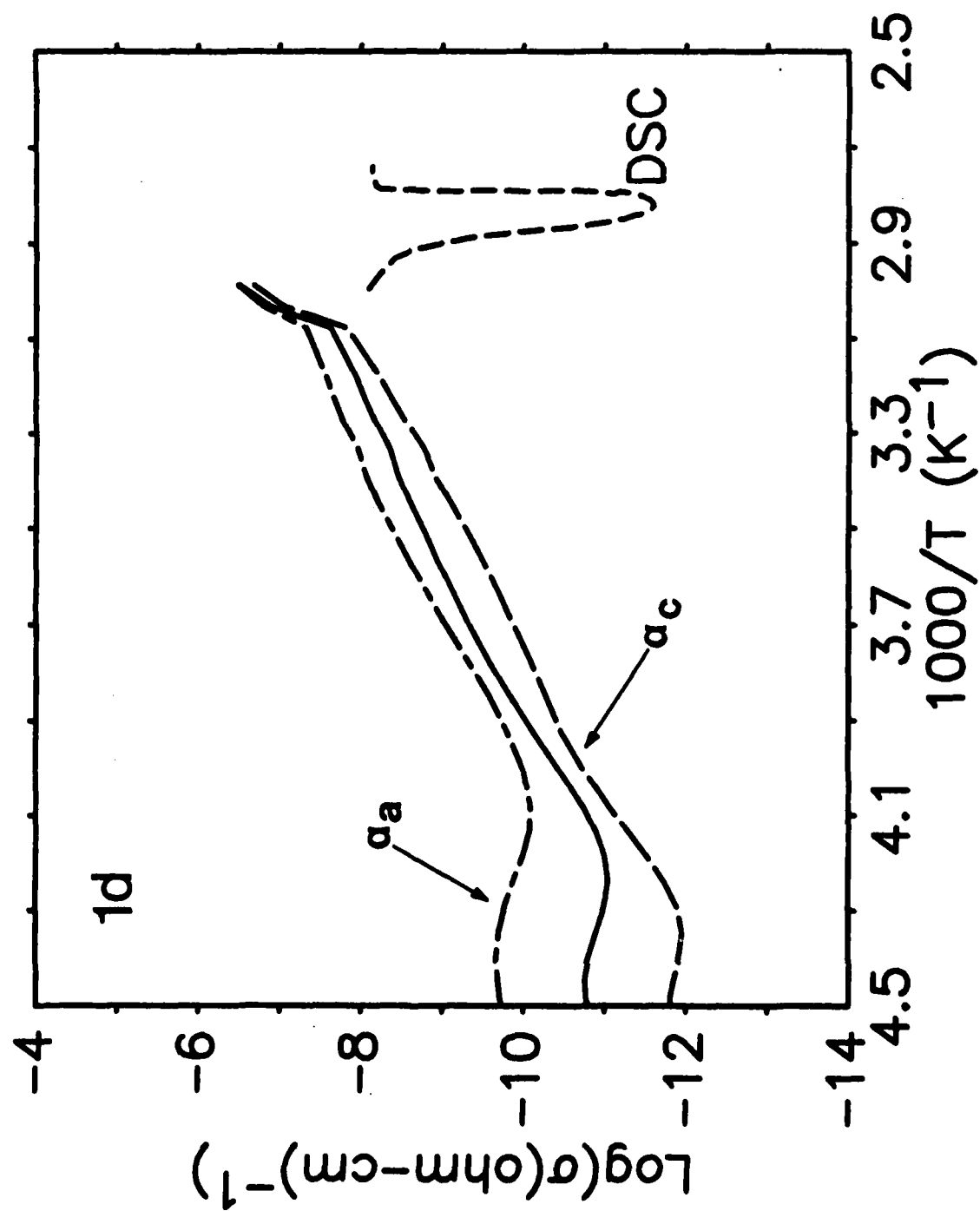
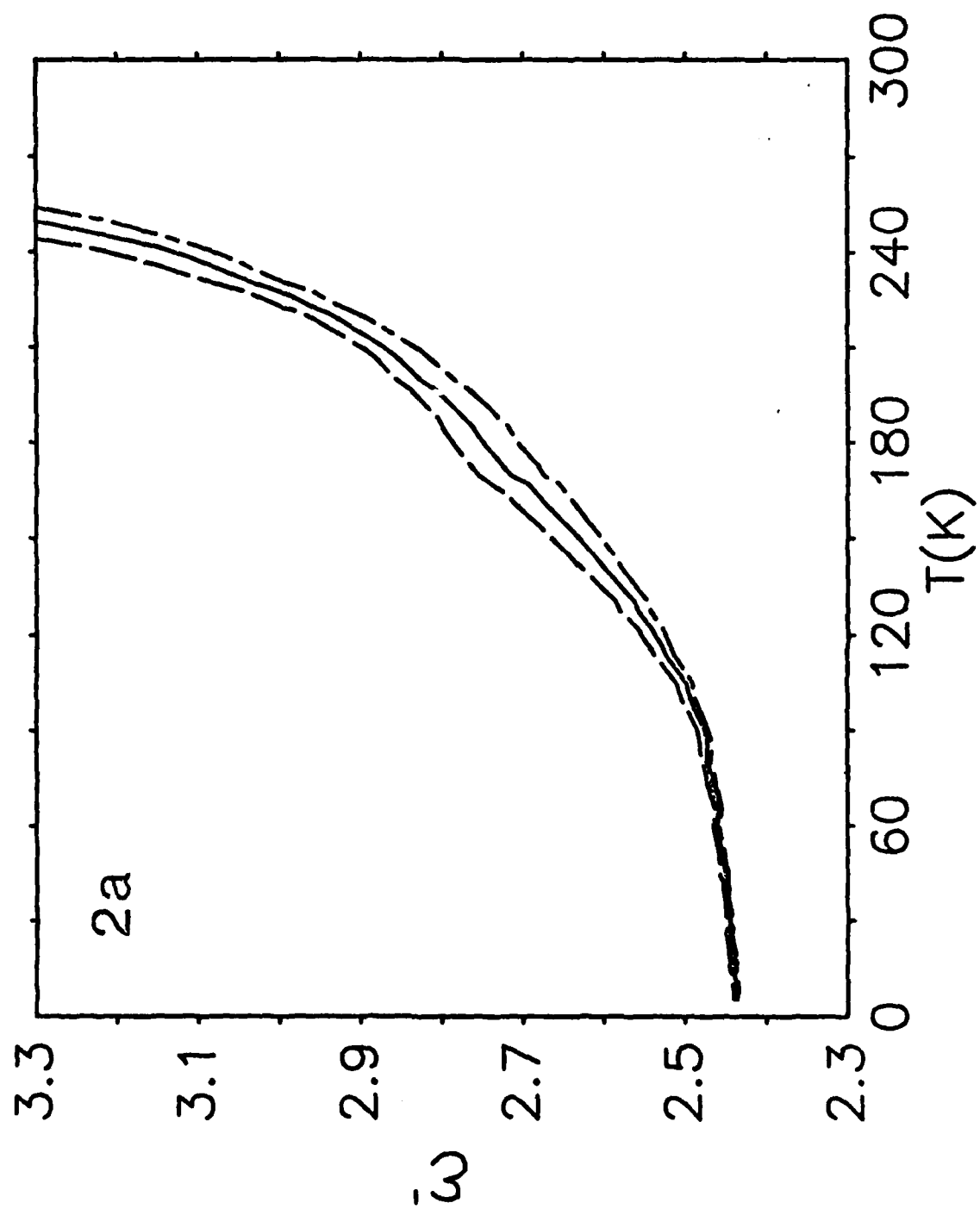
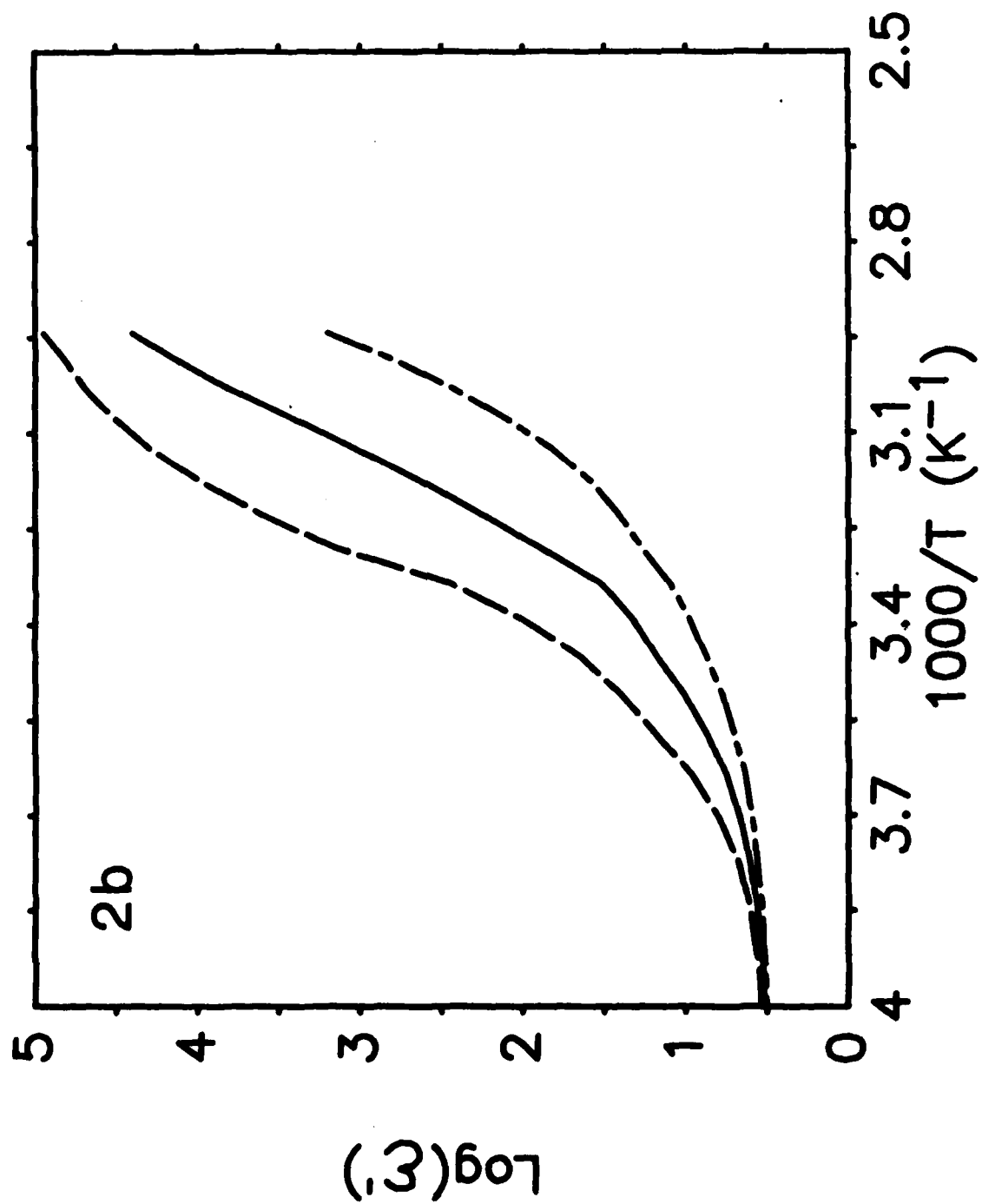
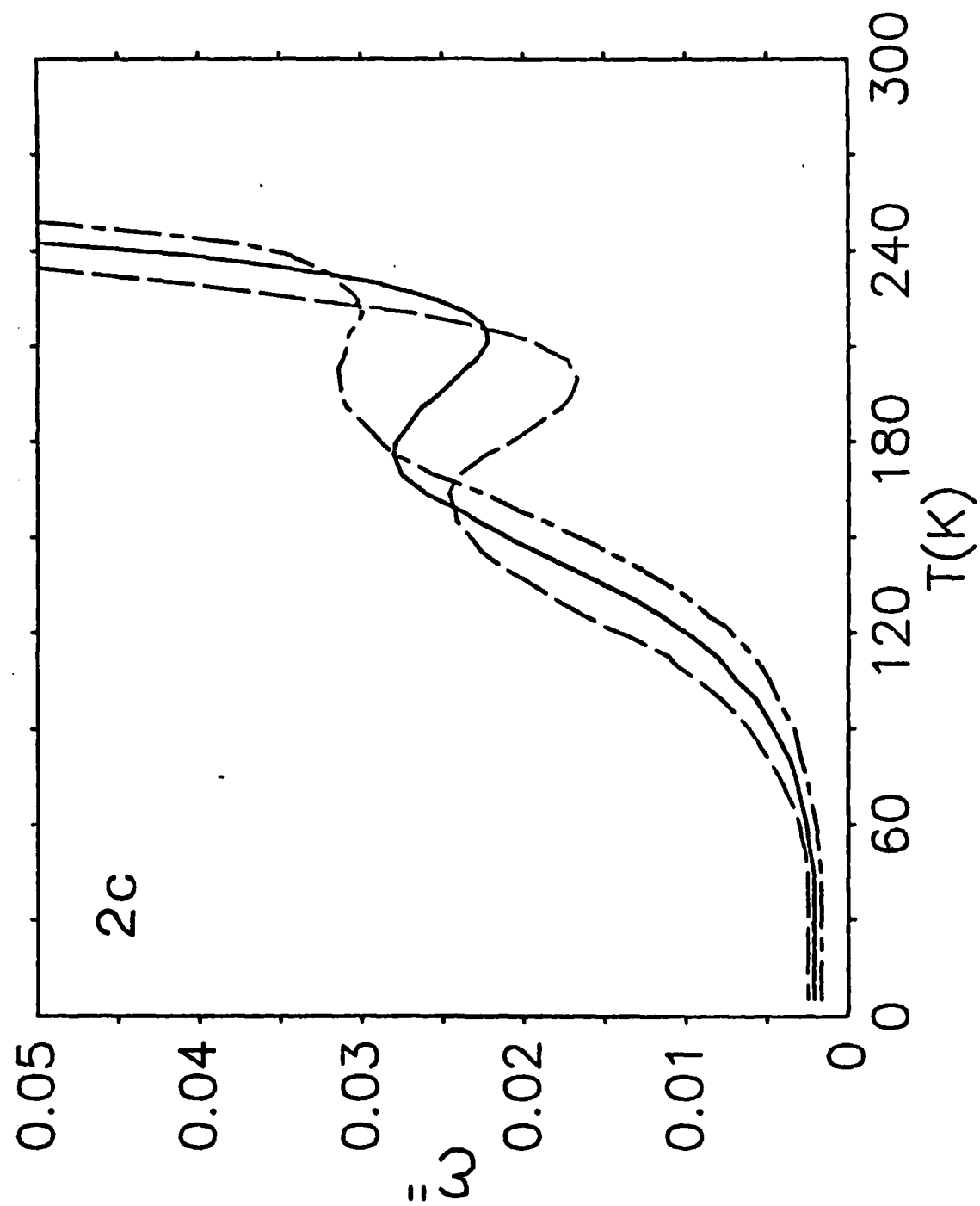


Fig. 2. PEO₅-LiSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz. The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. $T(K)$ (b) $\text{Log}(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. $T(K)$ (d) $\text{Log}(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC discontinuity of 5 units.







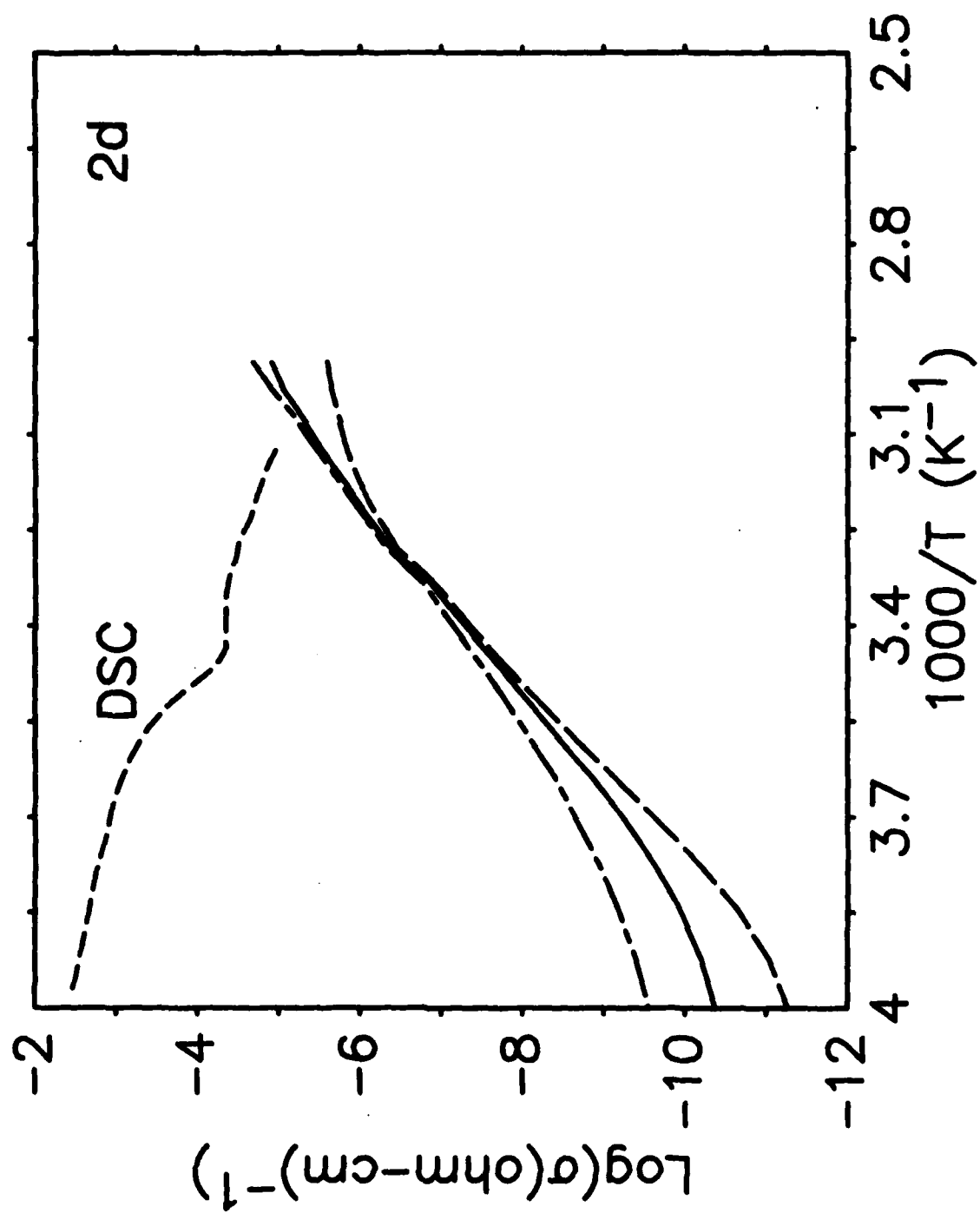
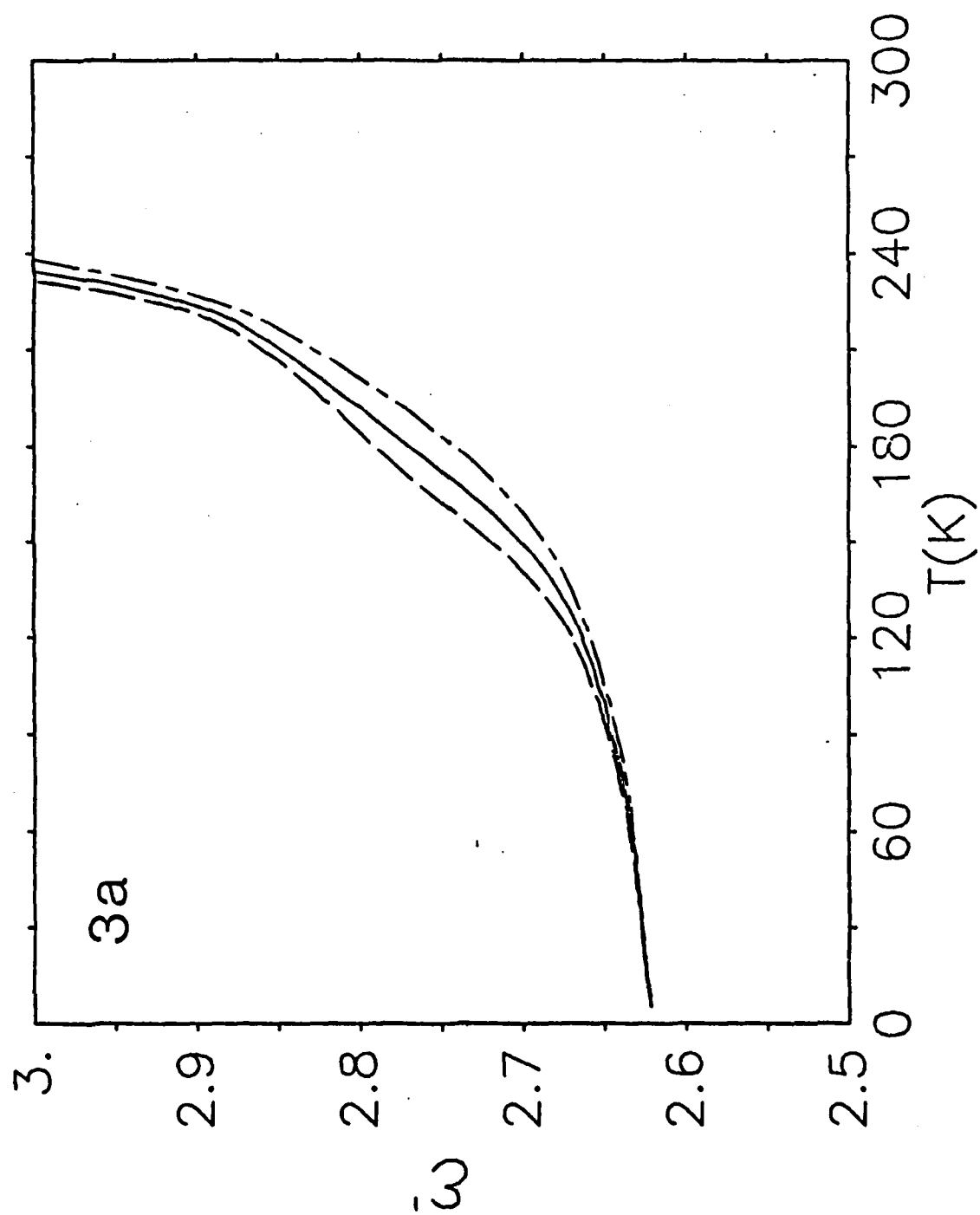
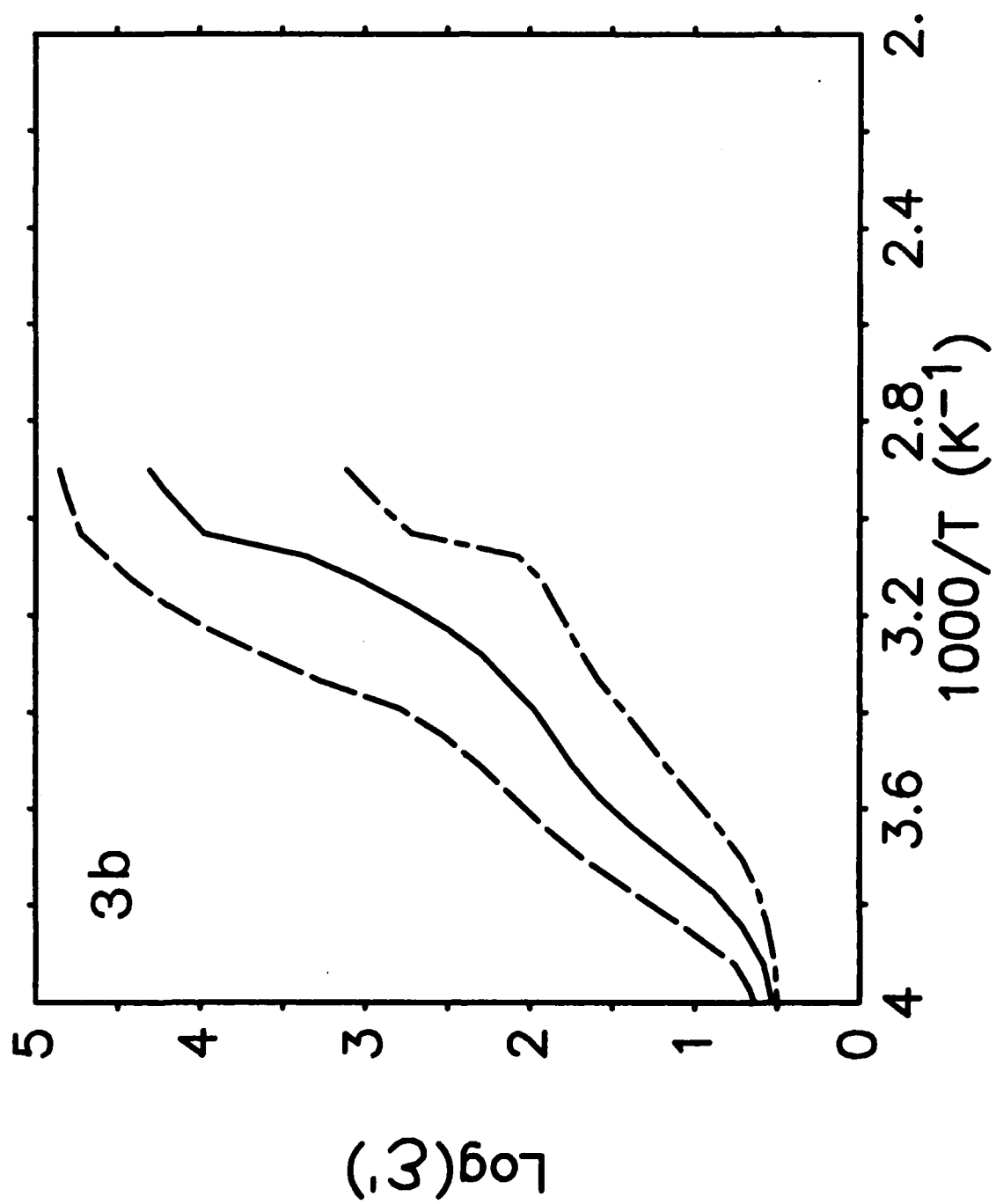
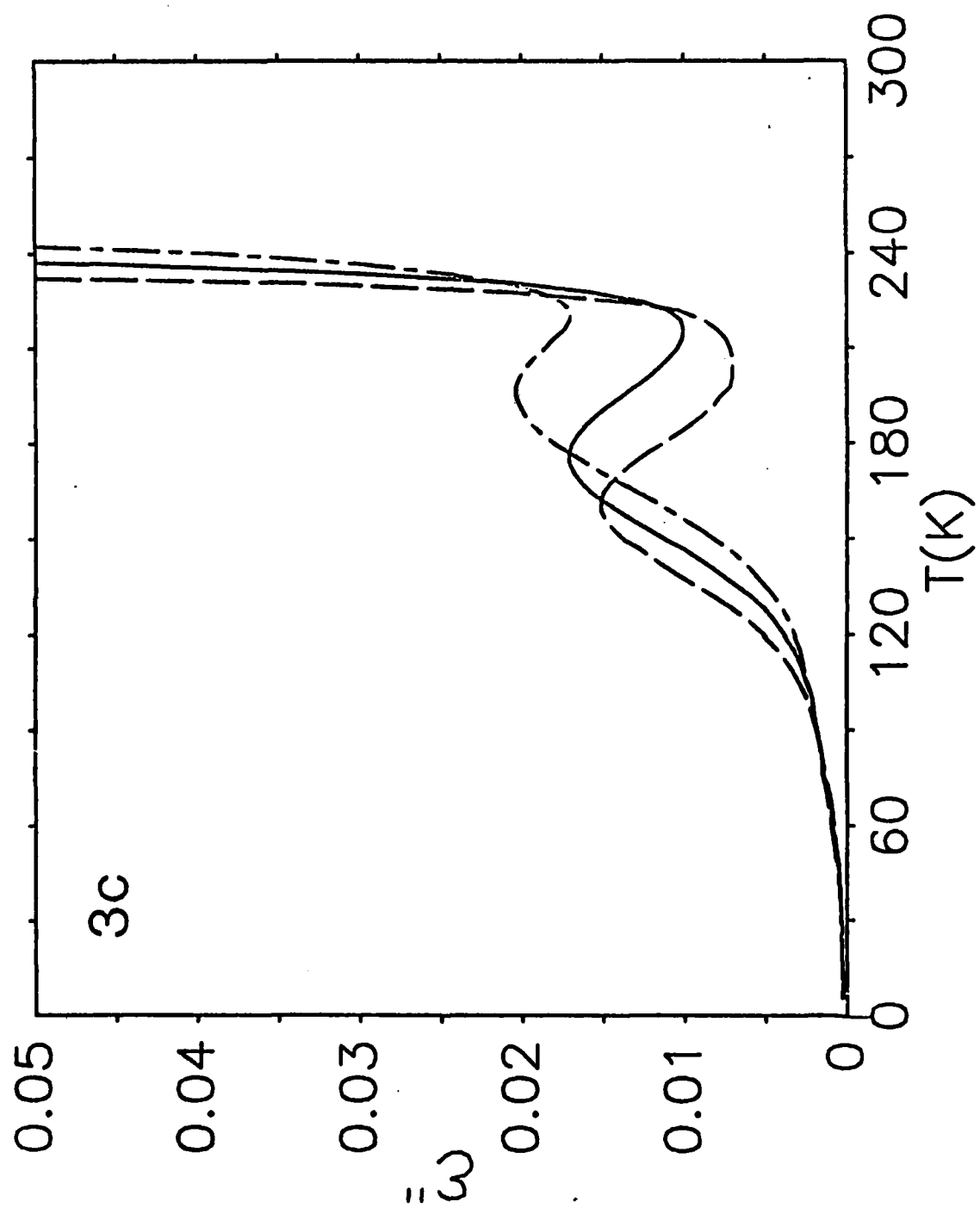


Fig. 3. PEO_{4.5}-NaSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz; + data of Wright (2). The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. $T(K)$ (b) $\text{Log}(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. $T(K)$ (d) $\text{Log}(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC peak height of 2 units.







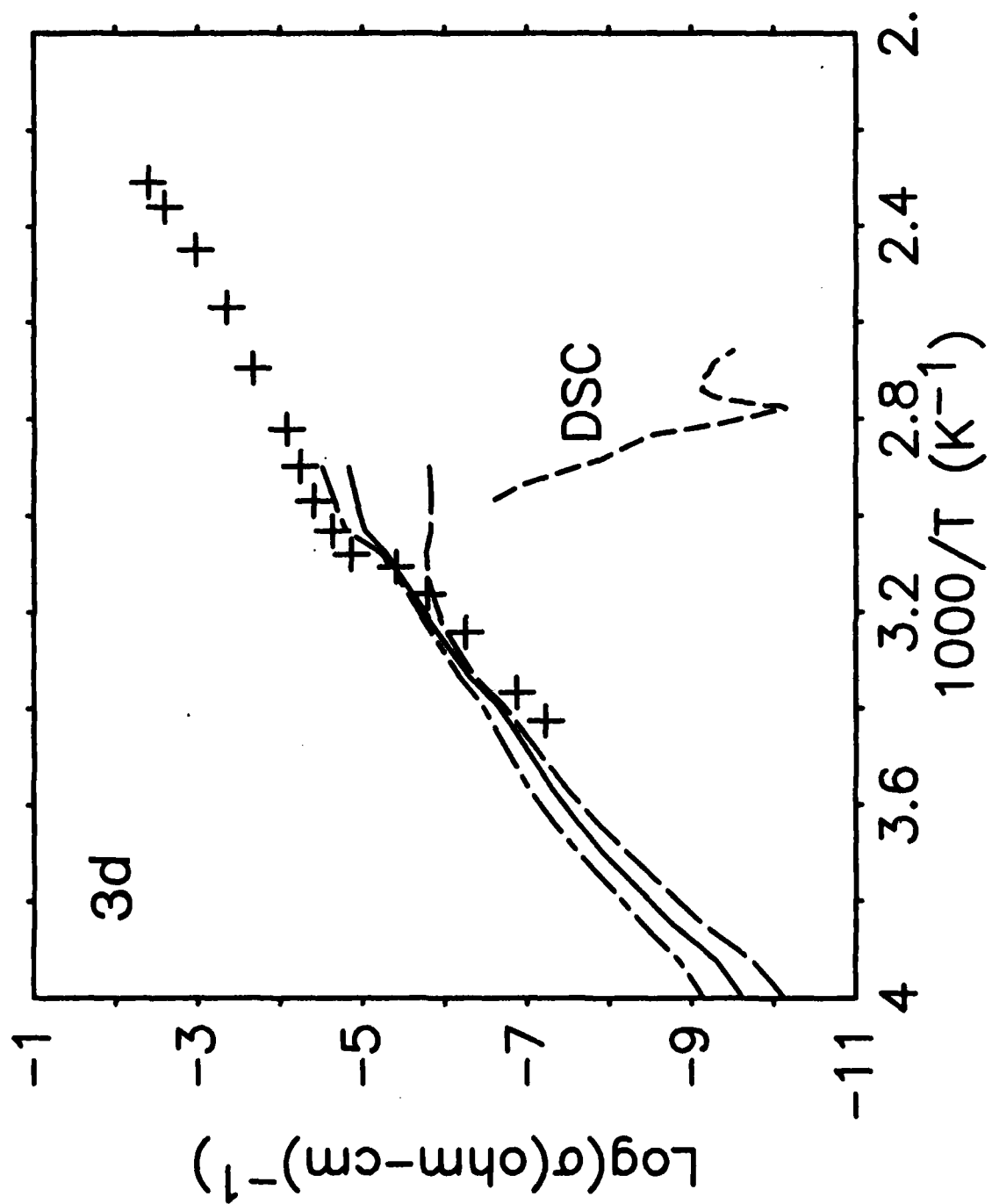
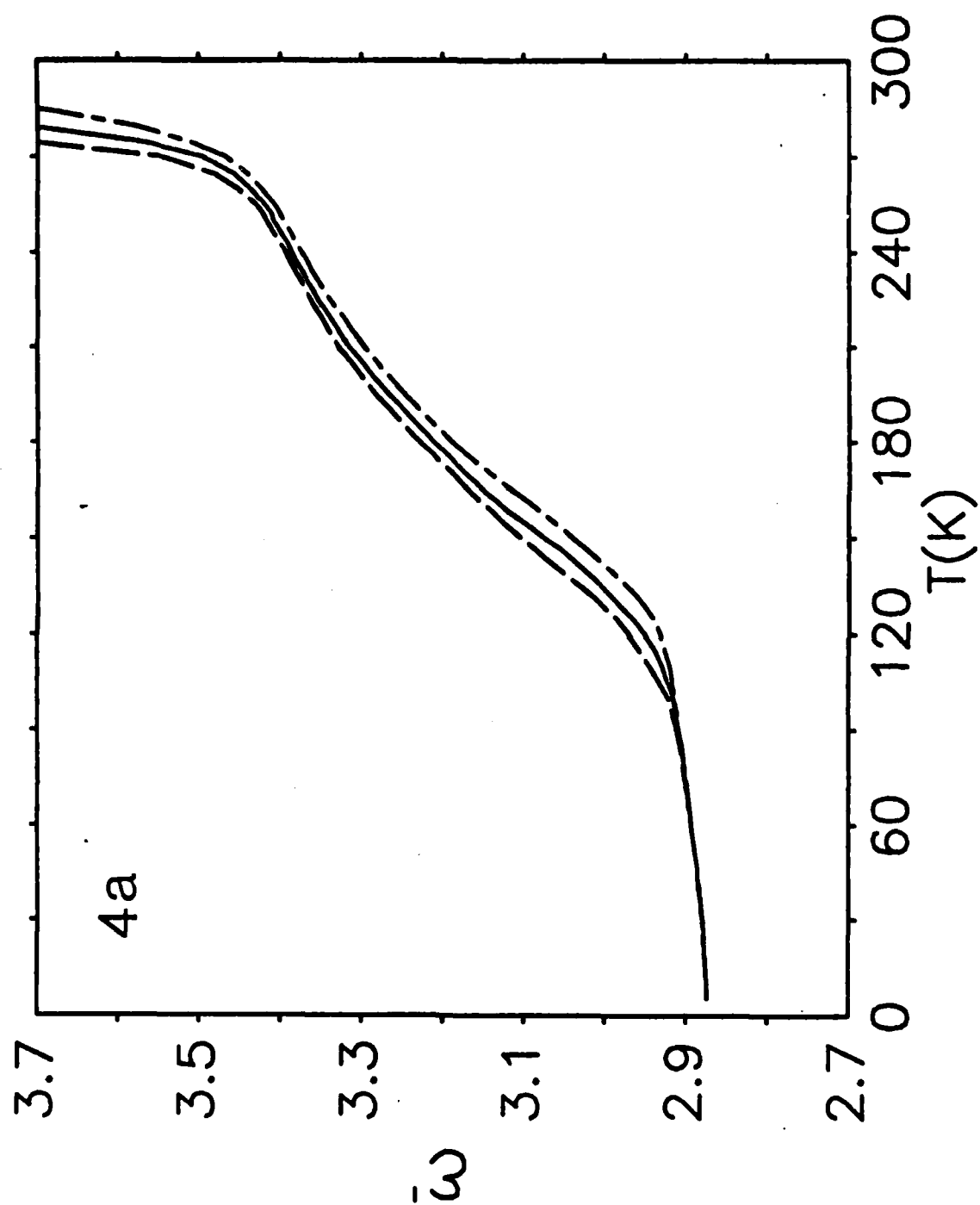
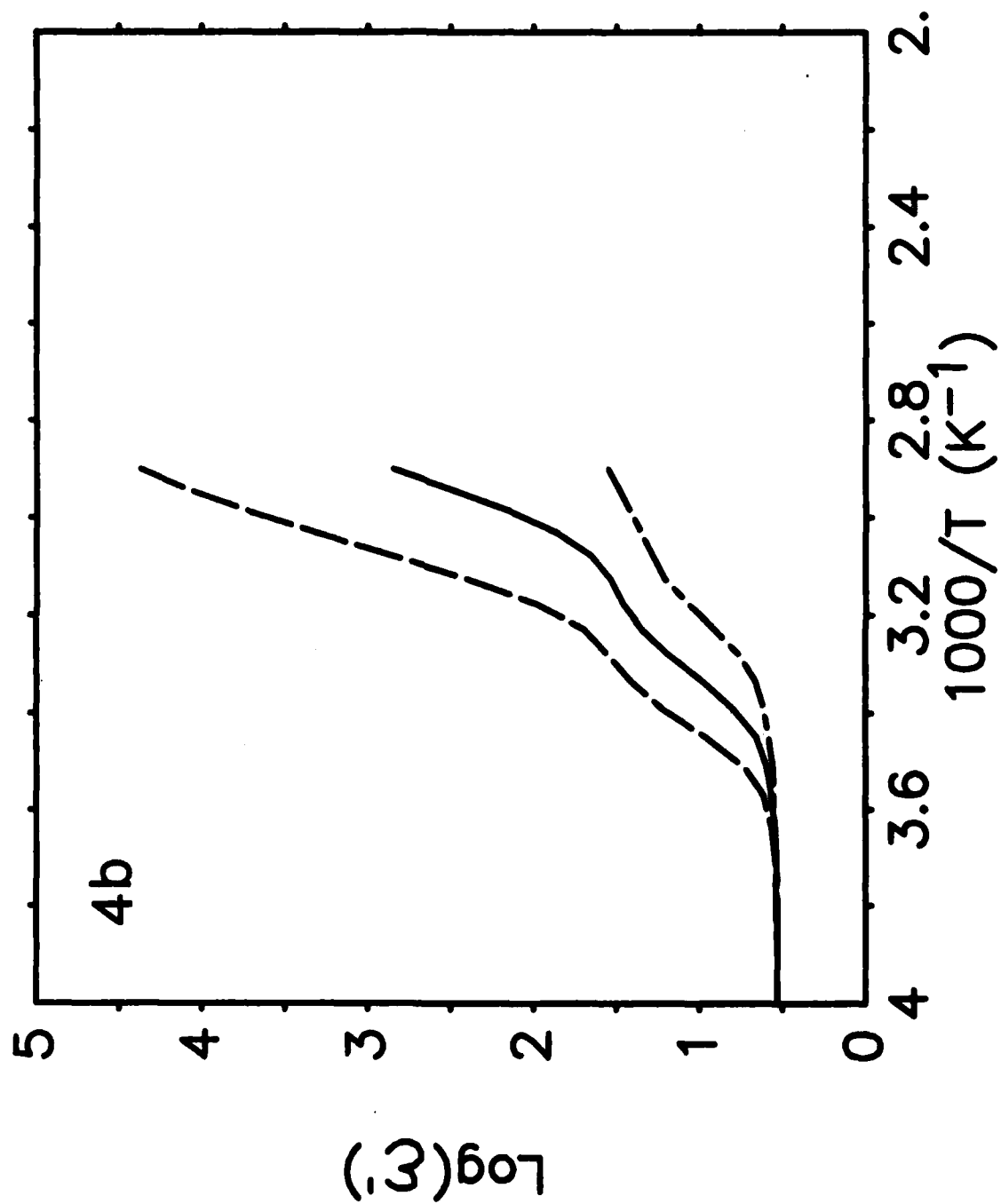
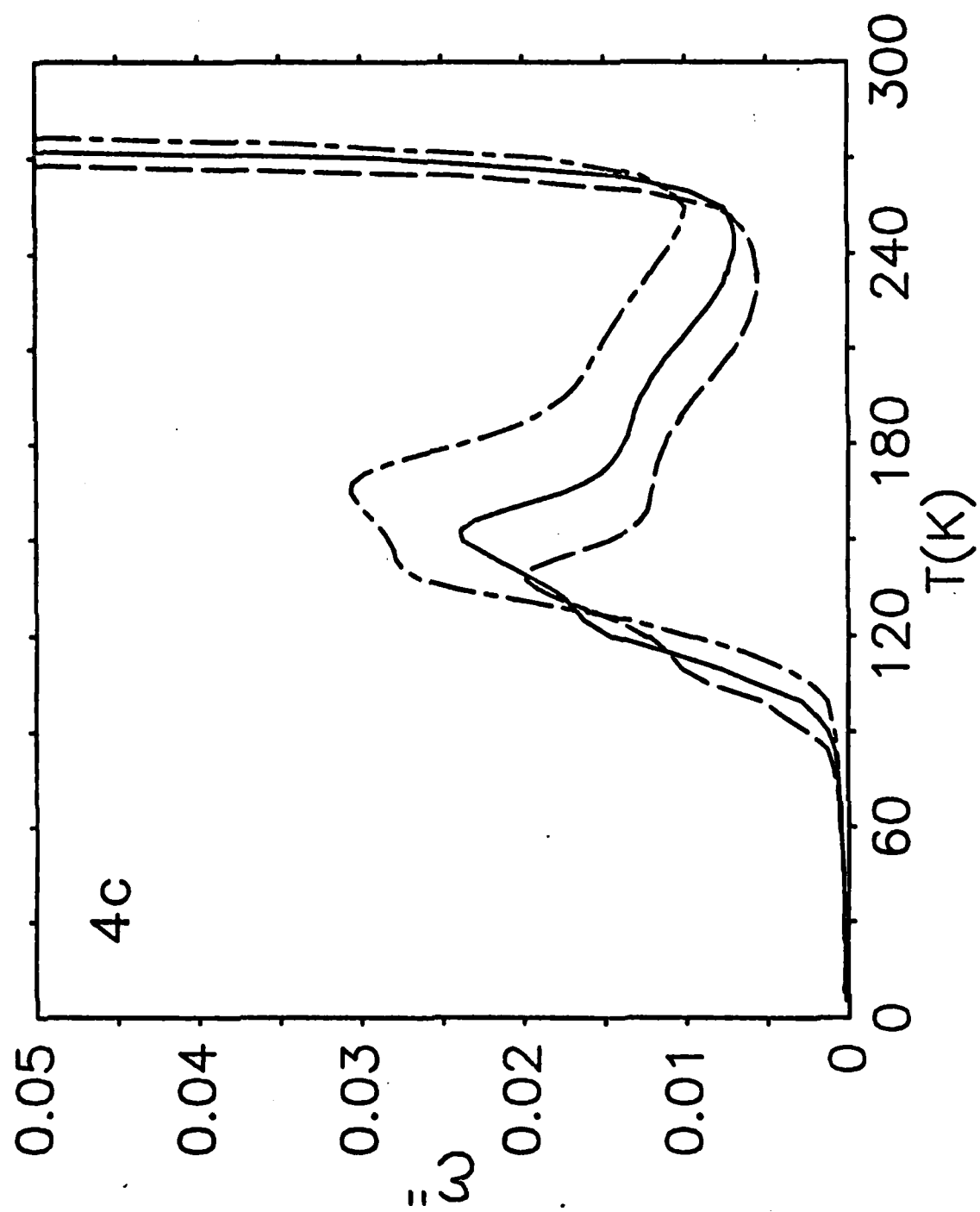


Fig. 4. PEO_{4.5}-KSCN. The dielectric data are: dashed curve 100 Hz; solid curve 1000 Hz; chain link curve 10,000 Hz; + data of Wright (2). The dielectric data are for decreasing temperatures only and straight lines connect the datum points. The DSC results are for increasing temperatures at a rate of 10C per minute. (a) ϵ' vs. $T(K)$ (b) $\text{Log}(\epsilon')$ vs. $1000/T(K^{-1})$ (c) ϵ'' vs. $T(K)$ (d) $\text{Log}(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(K^{-1})$; DSC peak height of 28 units.







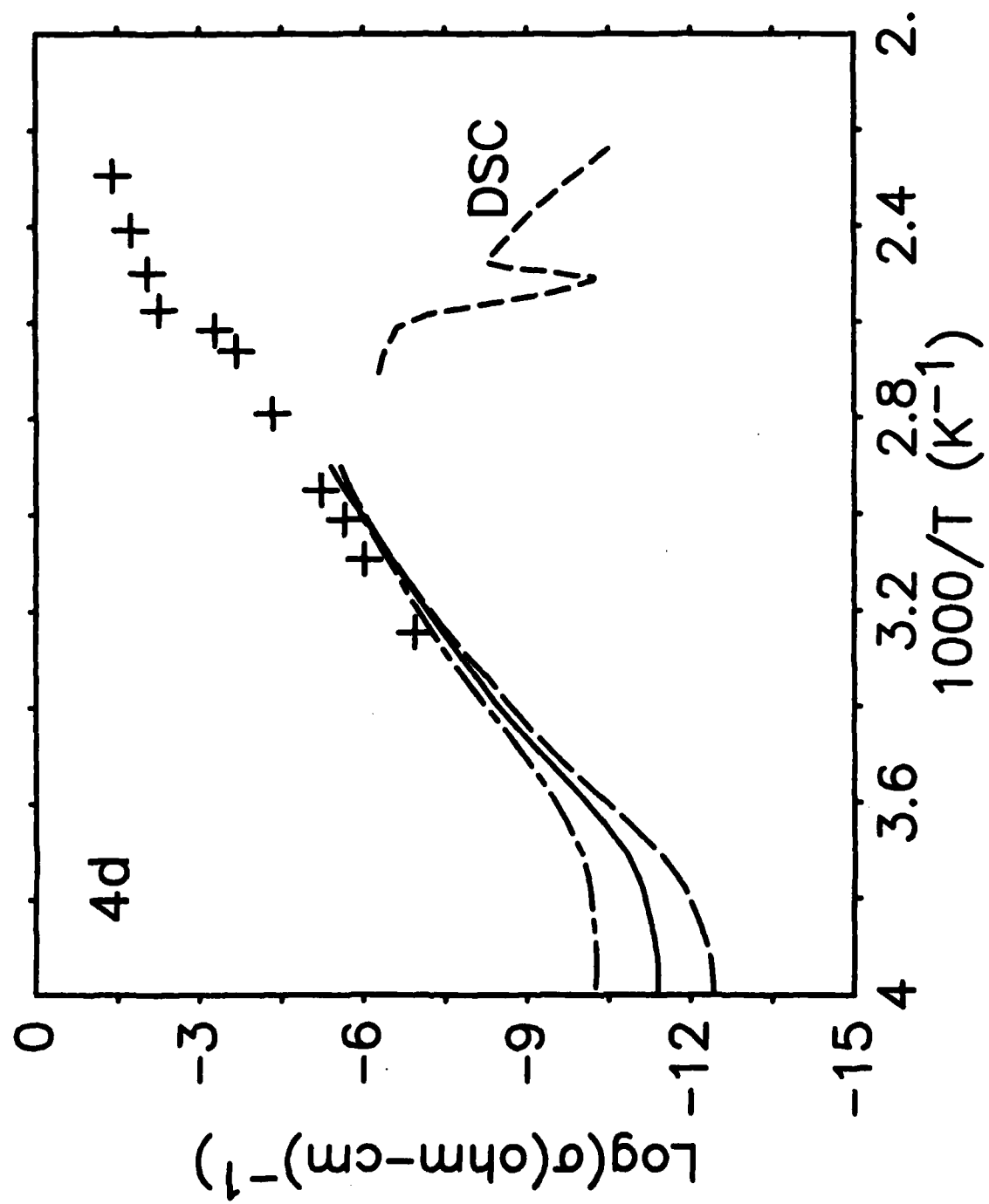
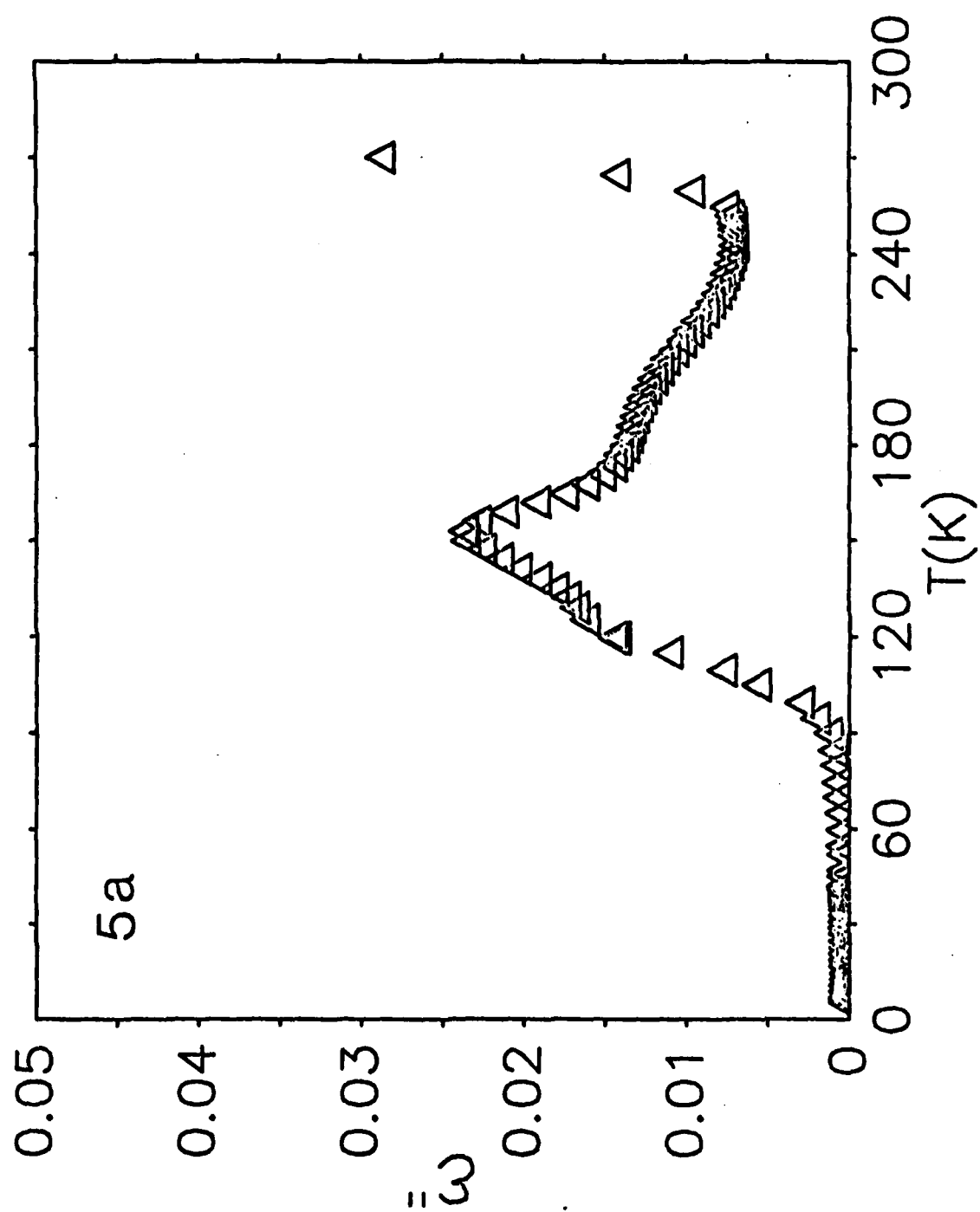
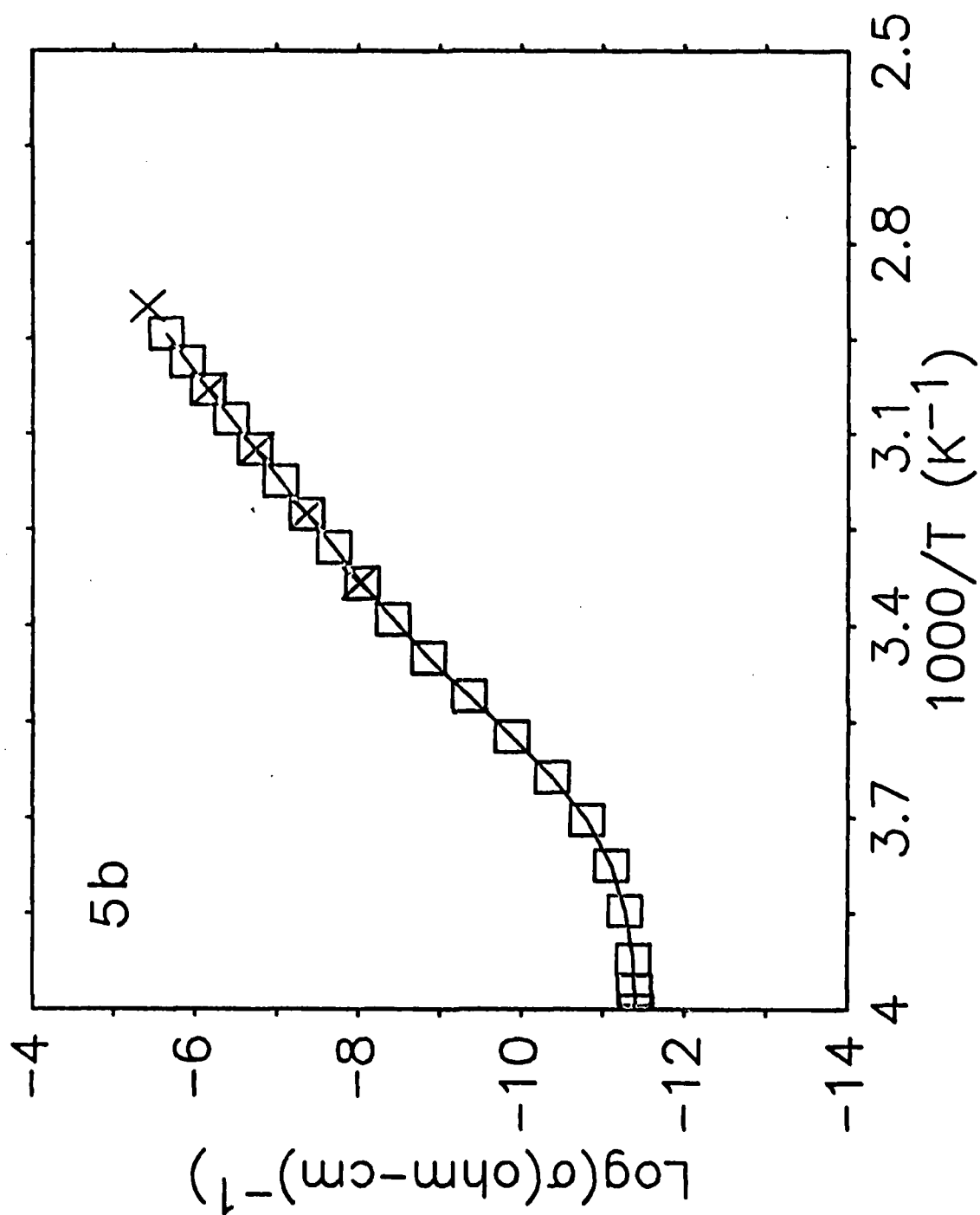


Fig. 5. $\text{PEO}_{4.5}\text{-KSCN}$. (a) ϵ'' vs. $T(\text{K})$ at 10^3 Hz. The datum points are represented by triangles.
 (b) $\text{Log}(\sigma(\Omega\text{-cm})^{-1})$ vs. $1000/T(\text{K}^{-1})$ at 10^3 Hz. x - Increasing temperature; o - Decreasing temperature. Straight lines connect the datum points.





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that water may enhance the formation of amorphous complexed PEO. In pure PEO, α_a and γ relaxations are observed in good agreement with previous work. A thermal anomaly is found corresponding to α_a . In addition, α_c is identified in pure PEO. Very little difference is found for the γ relaxation between pure PEO and PEO-LiSCN and PEO-NaSCN. For PEO-KSCN, three distinct peaks are found in the γ relaxation region. These results are consistent with a $tg^+t \rightleftharpoons tg^-t$ transition interpretation for γ where the cations reside within the helical channels at low temperatures.