20030205241

(2)

UNCLASSIFIED MASTER COPY - FOR REPRODUCTION PURPOSES

SECURITY CLASSIFICATION OF THIS PAGE

# REPORT DOCUMENTATION PAGE

DTIC ELECTE JUL 31 1989 B

AD-A210 797

1a. REPORT SECURITY CLASSIFICATION: Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.

5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 23230.2-LS-A

6a. NAME OF PERFORMING ORGANIZATION: Albert Einstein Medical Center

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)
York and Tabor Roads
Philadelphia, PA 19141

7b. ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-85-K-0243

8c. ADDRESS (City, State, and ZIP Code)
P. O. Box 12211
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

| PROGRAM ELEMENT NO | PROJECT NO | TASK NO. | WORK UNIT ACCESSION NO |
|---|---|---|---|
|  |  |  |  |

11. TITLE (Include Security Classification): Synthetic polypeptide composites for sensor applications

12. PERSONAL AUTHOR(S): Drs. S. Erhan, E.L. Cross and A. Bhalla

13a. TYPE OF REPORT: Final

13b. TIME COVERED: FROM 11/1/[illegible] TO [illegible]/30/89

14. DATE OF REPORT (Year, Month, Day): 1989, July, 10

15. PAGE COUNT: 71

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES

| FIELD | GROUP | SUB-GROUP |
|---|---|---|
|  |  |  |
|  |  |  |

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Polypeptide, synthetic, gelatin, sensor, pyroelectric, piezo electric, dielectric

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Due to technical difficulties, i.e., insolubility of theproducts, emphasis has been placed on modification of gelatine, a very highly polar molecule, while trying to find a satisfactory solution to solubility problems. The modified gelatins have performed exceptionally well: even at this early stage samples show under bias response comparable to best polar polymer (PVF$_2$) and competitive with the inorganic $LiTaO_3$.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION: Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

# SYNTHETIC POLYPEPTIDE COMPOSITES FOR SENSOR APPLICATIONS

## FINAL REPORT

Drs. S. Erhan, E.L. Cross and A. Bhalla

7/10/89

U.S. Army Research Office

Contract DAAG29-85-K-0243

Albert Einstein Medical Center
York and Tabor Roads
Philadelphia, PA 19141

# I. INTRODUCTION

Over the period of this contract (June 1986 to June 1989) major work has been undertaken upon the following research topics:

(1) Synthesis of synthetic polypeptide structures;
(2) Modification of natural gelatin structures to incorporate mobile dipolar species;
(3) Dielectric analysis of high dielectric permittivity liquids;
(4) Dielectric analysis of gelatin and of modified gelatin-based compositions;
(5) Pyroelectric analysis of the gelatin-based systems using Byer-Roundy method of analysis;
(6) Development of a new type of Chynoweth system for measuring the "true" AC pyroelectric response;
(7) Confirmation of high true pyroelectricity in the modified gelatins under DC bias fields; and
(8) Preliminary evaluation of artificial Maxwell Wagner bilayer structures.

Work on the synthesis of different compositions, the development of pinhole free thin films of the gelatin-based systems and the casting of composite layer structure Maxwell Wagner solids was carried out at the Albert Einstein Medical Center under the direction of Dr. S. Erhan. All property measurements, including dielectric spectra as a function of temperature, frequency and field, and pyroelectric response using both DC and AC measuring techniques were carried out in the Materials Research Laboratory at Penn State under the joint direction of Dr. A.S. Bhalla and Dr. L. Eric Cross.

In this report, the preparative studies are presented in Section 2, dielectric studies as a function of frequency, temperature and electric bias field in Section 3, and the pyroelectric studies including the rationale for the new Chynoweth AC technique are given in Section 4. Section 5 highlights the preliminary findings from measurements on some simple bilayer structures fabricated upon metal substrates. Section 6 discusses the research findings and some models which may account qualitatively for the most unusual and interesting electrical properties of the gelatin-based systems. In Section 7 avenues for potential future studies on these systems are explored.

It was realized at the outset that the task of synthesizing completely new polar polypeptides was highly speculative and that the synthesis routes were largely unexplored. Over the first year of the contract it was realized that because of solubility problems even the polypeptide which could be synthesized were not in a form which could be measured. Attention was then concentrated on the natural gelatin systems and upon modes of modification which could give rise to highly polar but dielectrically "soft" structures. This change happened also at the time when in the application community for new pyroelectrics it was realized that a switchable (polable) material has many potential advantages permitting much simpler matrix switching of the pixels in a CCD interrogated array structure. Even at this early stage in research it is exciting to realize that the samples show under bias response comparable to the best polar polymer (PVF2) and competitive with the inorganic $LiTaO_3$ which is widely used in point detectors.

## 2.1 Synthesis of Controlled Sequence Polypeptides:

2.1.1 N-carboxy anhydrides procedure, although very well studied, is unsuitable for synthesis of large quantities in acceptable yield.

2.1.2 Triphenyl phosphite catalyzed synthesis is quite satisfactory in providing acceptable yields.

2.1.3 Suitably modified, i.e., with 2.4 dihydroxybenzaldehyde, homopolymers such as polylysine become insoluble in all solvents except acids which limit usefulness.

2.1.4 Also efforts are being made to partially modify the polylysine and treat the modified polylysine with nitrous acid to obtain a more soluble product according to attached scheme

2.1.5 Studies are concentrated in a systematic search to identify combinations of amino acids that will yield soluble peptides that will still have sufficiently high dipole moments after modification.

## 2.2 MODIFIED GELATINS

Since resorcinal is amolecule with a very high dipole moment we have modified gelatin, using 2,4-dihydroxybenzaldehyde and other molecules that are likely to have a high dipole moment; 4-nitro and 2,4-dinitrobenzaldehyde with reductive alkylation.

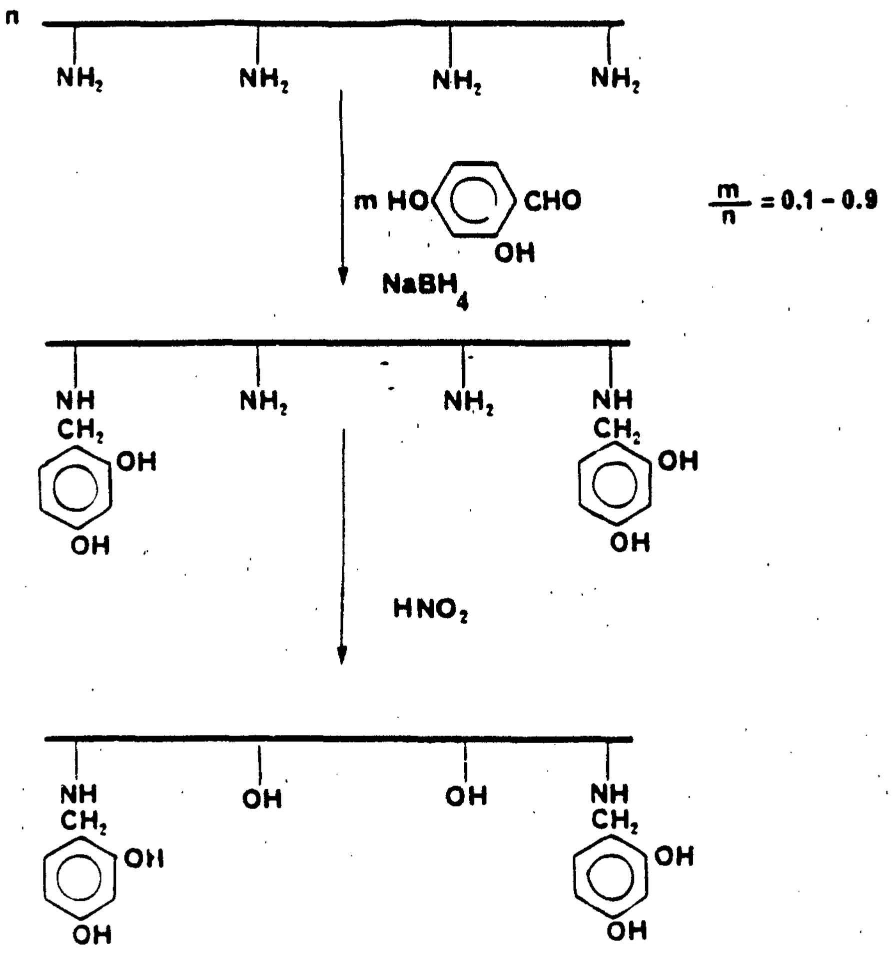
For the modification of gelatin backbone 5g gelatin corresponding to 200 mg of lysine (1.408 mM) was dissolved

70 cm borax buffer (pH 7.2). Ten molar excess of sodium cyanoborohydride were dissolved in 70 $cm^3$ of DMSO and were added to gelatin solution, dropwise, under constant stirring and at room temperature for 30 min. The mixture was stirred for 5 h, the mixture was acidified with 6 M HCl to destroy unreacted cyanoborohydride and was precipitated by pouring into acetone. The precipitate was washed several times with acetone and was either dialysed against 0.006 M acetic acid or passed over Biogel P-2 colum to remove unreacted low molecular weight reagent traces.

Because our earlier studies have demonstrated that reductive alkylation can only modify about 60% of available lysines, and because these unreacted lysines were attacked by epichlorohydrin, we have also reacted 2,4-dihydroxybenzaldehyde modified gelatin with epoxidized polyglycerin.

The modified gelatins as well as polylysine were cast into films after dissolving them in water, in teflon covered trays. A typical example is given for 2,4-dihydroxybenzaldehyde modified gelatin films:

4 g modified gelatin was dissolved in 300 ml double distilled water, by warming, approximately 60°C. The solution was filtered through glass wool and degassed for 15' under vacuum. It was poured into a teflon tray and allowed to dry in a dust-free hood.


n
NH2
m HO CHO OH
m/n = 0.1 - 0.9
NaBH4
NH CH2 OH OH
HNO2
OH

# 3. DIELECTRIC STUDIES

## 3.1 High Dielectric Permittivity Liquids

### 3.1.1 Introduction

Over the first three months of the contract, while the attempts were underway to synthesize the polypeptides in highly oriented polar form, it was decided to test out the techniques for dielectric studies upon organic systems by exploring a range of high permittivity formamide liquids, measuring over the freezing range in these glassy systems to examine the possibility of poling in pyroelectric forms at low temperature.

### 3.1.2 Liquids Under Study

Following earlier work from Japan it was decided to explore liquids based on formamide ($HCONH_2$), N methyl formamide ($HCONHCH_3$) and NN dimethyl formamide ($HCON(CH_3)_2$). First the pure liquids were measured over the temperature range from -100° to +50°C for frequencies from 100 Hz to 100 KHz using the H.P. automatic testing system.

The liquids were contained in a simple coaxial sample holder between platinum electrodes. After filling, the sample holder was sealed to prevent contamination with moisture.

Data for pure formamide are summarized in Figs. 1a, b which show $\varepsilon'$ and tan $\delta$ over the full temperature/frequency range. Above 0°C the permittivity is extremely high ($10^4$-$10^6$) and strongly dispersive. The response appears to freeze out over the range from -50° to -20°C exhibiting sharp high maxima in tan $\delta$ in this range (1b). Taking the temperature of tan $\delta$ maximum as a function of frequency to represent the mean relaxation time J the log J vs. 1/T plot is quite linear, but the slope is a little different on cooling and heating yielding an activation energy for the relaxation between 1.1. and 1.2 eV (Fig. 2). It seems probable from Fig. 1a that the transition near 0°C may be a melting and careful measurements on slow cooling (Figs. 3a, b) confirm over 20°C of supercooling associated with the transition. It is interesting to note however that melting/freezing does not eliminate the relaxing component of the response which freezes out at lower temperature.

For N methyl formamide dielectric data are presented in Figs. 4a, b. Again the cooling curves exhibit strong supercooling but the very high K ($10^3$ to $10^6$) is again not lost on freezing, but freezes out over a temperature range down to -60°C. On both cooling and heating the relaxation time does not follow a clear linear log $\tau$ vs. 1/T (Fig. 5) plot and now "best fits" yield activation energies of 0.47 eV (cooling) and 0.74 eV (heating) clear evidence of a more complex polarizability. For NN dimethyl formamide, the freeze out is at even lower temperature but the permittivity is now also significantly smaller ($10^2$ to $10^4$ $\varepsilon_0$). Now the relaxation process is highly modified by the freezing behavior (Figs. 6a, b) and it is impossible to deduce an activation energy from the behavior.

In mixtures of normal and methyl formamide it appears that the relaxation features of each liquid are preserved suggesting that what is being observed is a truly molecular dipole phenomenon data for 5:1, 2:1, 1:1 and 1:2 mixtures are given in Figs. 7a, b, 8a, b, 9a, b, 10a and b, respectively. For formamide:dimethyl formamide mixtures are given in Figs. 11a, b and Figs. 12a, b, respectively, again it is easy to see that qualitative features of the two spectra largely preserved with relative ratios changing with the volume concentrations.

## 3.2 Dielectric Measurements on Gelatin-based Compositions

### 3.2.1 Introduction

Since it was proving exceedingly difficult to produce synthetic polar peptides in a form suitable for dielectric study, the original concept was modified to explore the properties of castable gelatin films which could then be chemically modified to introduce highly dipolar groups. Early measurements showed that the gelatin itself provided a host which had moderate permittivity only weakly dispersive over the temperature range from -150°C to +40°C with tangent $\delta$ values less than 0.10 over the whole temperature and frequency range.

In all, some 20 differently modified gelatins synthesized at Albert Einstein Medical Center were received and measured for dielectric response as delineated in the following section.

### 3.2.2 Measurements

(a) Weak Field Permittivity. Permittivity and loss as a function of frequency and temperature for a simple non SH gelatin are shown in Figs. 13a, b. Measurements on several other lots, and on samples of SA gelatin give qualitatively similar results with ranges of $\varepsilon_{max}$ at room temperature over the range from 8 to 15 at a frequency of 10 Hz.

Films modified with 2.4 dihydroxy benzaldehyde (DHBA), a very strongly polar molecule, gave the lowest room temperature relaxation frequency 20 Hz with a dielectric permittivity of 250 $\varepsilon_0$ at 10 Hz, Figs. 14a, b. For the DHBA modified sample permittivity as a function of temperature shows a massive low frequency (100 Hz) dielectric peak (~100,000) at 43°C which is strongly dispersive over the range from 100 Hz to 100 KHz. The tan $\delta$ exhibits a most interesting double peak response at the lower frequency, the peaks corresponding as expected to the steeply rising and steeply falling sections of the real part of $\varepsilon$, Figs. 15a, b.

In a 2.4 dihydroxy benzaldehyde sample modified with epi-triglycerin the relaxation frequency is raised to 100 Hz and only one relaxation is evident (Fig. 16). Again the permittivity vs. temperature exhibits a very strong maximum now at 45°C with double humps in tan $\delta$ at low frequency, which coalesce into a single peak at high frequency (100 KHz), Figs. 17a, b.

For a 4 nitrobenzaldehyde modified gelatin the relaxation peak at room temperature is raised to 190 Hz with a low frequency (10 Hz) value for $\varepsilon'$ of over 2,000 (Figs. 18a, b). In the nitro-modified material the peak in $\varepsilon'$ is again near 45°C, but now the low frequency value of $\varepsilon'$ is much reduced (~50) and the $\tan\delta$ curves show only a single maximum again near 45°C (Figs. 19a, b). For 2-4 dinitrobenzaldehyde modified gelatin the relaxation peak is raised to 650 Hz at 22°C with $\varepsilon'$ approaching 4,000 at 10 Hz (Figs. 20a, b). Again the permittivity vs. temperature shows a sharp peak near 40°C with a lower maximum value ($\varepsilon' \sim 70$) and only a broad single peak in $\tan\delta$ at lower frequencies (Figs. 21a, b).

Triglycerin modified gelatin shows the highest room temperature value of relaxation frequency 6.5 KHz, very large values of $\varepsilon'$ (~300,000) at 10 HZ (Figs. 22a, b). Now in the dielectric response as a function of temperature there is evidence of separated double peaks both in the real pat of the response ($\varepsilon'$) and in the $\tan\delta$ (Figs. 23a, b).

The measurements listed above are a representative sampling of the weak field response for the 20 modified gelatins measured. Data for these and the other samples are tabulated in Table 1.

(b) <u>Dielectric Saturation Studies</u>. In view of the clear evidence of massive dielectric relaxation at room temperature for the modified gelatins at low frequency, suggesting large dipole moments it appeared desirable to see whether additional information could be obtained by measuring the dielectric saturation under increasing DC fields for the low frequency part of the permittivity.

Firstly, since the gelatin itself is only weakly dispersive one should expect little dielectric saturation and this is indeed the case even at low frequency (Figs. 24a, b). For the modified gelatins however, the behavior appears much more complex than can be accounted for by a simple non-associating dipole model.

In the triglycerin modified samples where the relaxation frequency $\omega_0$ (6.5 KHz) is well above the measuring frequency (500 Hz) the saturation appears normal (Fig. 25) and fits well to a Langevin function (Fig. 26) however the dipole moment required for the fitting appears anomalously large.

For gelatin modified with hexaglycerin, in spite of an apparently very large dielectric permittivity, the saturation is negligible even at 100 Hz (fig. 27). For a number of the films which show larger relaxation times, increasing DC field leads to increasing dielectric permittivity peaking at the higher field levels. An example is film 14 where the modifier is 2:4 dinitrobenzaldehyde (Fig. 28a) with $\tan\delta$ values following a pattern consistent with the real part (Fig. 28b).

## 4. PYROELECTRIC MEASUREMENTS

### 4.1 Introduction

Two well known techniques have been used to measure the pyroelectric response of the modified gelatin samples. The first is a simple Byer Roundy constant heating rate method which measures the total polarization in the sample including all trapped charge. The second is a modification of the AC Chynoweth method in which the sample is heated by a chopped infrared radiation absorbed at the surface and the AC current generated is measured. In this case, the calibration uses a standard material of identical geometry.

### 4 2 Measurement Techniques

(a) The Byer-Roundy Method. The Byer-Roundy Method is in principle very simple and is illustrated in schematic form in Fig. 29. The sample in the form of a thin plate equipped with metal electrodes on the major forces is placed in a computer-controlled oven. The over is programmed to a constant linear heating rate; in the MRL system this is 3°C/minute. As the polarization in the sample decreases with temperature a current is generated. This pyroelectric current ip is related to the pyroelectric coefficient p(T) by

$$p(t) = \frac{ip}{A\partial T/\partial t}$$

The current ip is measured by a Hewlett Packard picoammeter and is recorded on the Y axis of an X:Y plotter whose X axis plots the sample temperature. The ip is also integrated over temperature T to give the polarization in the sample.

To run the experiment, the sample is poled under a high DC field applied as the sample is cooled down from room temperature to -150°C. The poling field is then disconnected, the sample momentarily short circuited, then the constant heating rate is started and the pyroelectric current measured.

(b) AC Chynoweth Method. The AC Chynoweth method is also quite simple in concept and is illustrated in Fig. 30. The sample, mounted upon a thermally isolating substrate is subjected to an AC heat signal by chopping radiation rom an infrared heat source. The AC pyroelectric current is measured after amplification in a preamplifier/impedance converter through a phase locked amplifier locked to the chopper frequency.

In the MRL Chynoweth system, which was built up and calibrated by J. Sopko as an MS thesis project in Electrical Engineering, local IR heating is provided through a multimode fiber optic link from a Seiko SMD 10E LED source driven by a Racal-Dana F-47 Function Generator (Fig. 31a). The sample is contained in an MMR variable temperature sample chamber controlled by a K.20 Temperature Controller. Pyroelectric current is amplified by a Model 181 Current/Voltage Amplifier which feeds either an EG and G 5208 lock-in analyzer or an HP 54201A Digitizing Oscilloscope each of which is locked to the function generator driving the LED source. The physical setup is shown in Fig. 31b.

Different sample configurations which can be used are illustrated in Figs. 32a, b and calibrated runs taken with $LiTaO_3$ and $LiNbO_3$ samples are given in Fig. 33.

### 4.3 Byer Roundy Measurements

Unmodified gelatin shows a pyroelectric current which peaks near 40°C at $\sim 10^{-1}$ C/°C/M$^2$ and an integrated charge which is rather flat over the range from -100° to 0°C then drops rapidly at higher temperature. Polarization levels are of order 1.6 c/M$^2$ (Fig. 34).

In the modified samples very well developed pyroelectric current peaks are observed in the temperature range from 10°C to 45°C and both the current levels and the integrated polarization are one to two orders larger than in the unmodified compositions. Typical examples are given in Figs. 35 to 39.

### 4.4 Chynoweth AC Pyroelectric Measurements

From the DC Byer Roundy measurements it is clear that very large polarizations can be induced in the modified gelatin systems using suitable DC bias fields. However the non-zero conductivity certainly makes one to suspect that a major fraction of the polarization may be due to trapped space charge. To distinguish true from this false pyroelectricity, it is important to use the AC method. During the AC heating the space charge is "walked out" of the system and is not replaced so that it does not contribute.

A second advantage of the AC method is that it does depend upon just those properties which control the very similar detector and IR imager applications.

(a) Room Temperature Studies. Samples were prepared in the form of thin disks 100 μ meters thick. Gold electrodes 5 mm in diameter were vacuum deposited and contacts made to the electrodes by fine gold wire cemented in place with air-drying silver. The surface was blackened by a paint on black with absorption coefficient $\eta \sim 0.98$.

For measurements the source was set to provide square pulses at a power level of 81.4 μ watt with the repetition rate varied from 0.5 to 10 pulses/second. Typical results for the Epi-decaglycerin modified sample (3) are presented in Table 2 and for the best sample, the triglycerin modified sample in Table 3.

In comparison, it may be noted that a $LiTaO_3$ disk 100 μ meter thick with an electrode 4 mm in diameter produced a relative sensitivity $R_i = 461.5$ μA/W. Thus the Epi-decaglycerin modified sample is clearly comparable to $LiTaO_3$ at 292°K whilst the triglycerin-modified sample is more than 5 times more sensitive.

(b) Pyroelectric Behavior as a Function of Temperature. The temperature dependence of the pyroelectric effect should be quite steep according to the Byer-Roundy results and this also proves to be the case for the Chynoweth method. Figure 40 shows data for the triglycerin-modified gelatin (sample 9) taken at a chopping frequency of 30 Hz, but a low bias of only 4.5 volts.

It may be noted that the peak response is now at 65°C significantly higher than the 10°C observed for Byer-Roundy. To compare with other polymer systems the data has been scaled to polyvinylidene difluoride PVF2, the strongest known pyroelectric polymer in Fig. 41. Even at low bias level, the triglycine-modified gelatin is almost as effective as PVF2.

## 5. PRELIMINARY OBSERVATIONS UPON BILAYER STRUCTURES

Observations at Einstein upon other programs have observed that protein forms very firmly adhering thin layers to a wide variety of metal substrates. Dielectric measurements on samples from Einstein have shown that the films have low dielectric loss and high resistivity (Figs. 42a, b).

To explore the possibility of generating on artificial Maxwell Wagner solid using the protein film in conjunction with a modified gelatin, several bilayer structures were developed by casting the gelatin on top of the film supported on a stainless steel or aluminum metal support. For the bilayer structure using a triglycerin-modified gelatin for the second layer, the major feature of the dielectric response i.e. the strong dielectric peak near 25°C is preserved, but now the loss levels are significantly lower with tan δ values less than 1.5. Again however, as in the original films, the double peak in the loss tangent is evident at low frequencies and merges back into a single peak at higher frequency (Figs. 43a, b).

Similar features have also been observed with hexa and decaglycerin-modified films although now the loss levels are significantly higher. We believe it will be interesting to explore a wider family of bilayer structures in which the thickness of each component is more carefully controlled so that a proper analysis can be made of the composite properties.

## 6. DISCUSSION

The early studies on high permittivity dielectric liquids highlight one of the major problems which is present to some extent in all the systems studied, i.e. the problem of ionic conductivity. Clearly the formamide family of liquids have very high permittivity ($10^4$ to $10^6\ \varepsilon_0$) at room temperature, and the response is dominantly dipolar, however, the high electrical conductivity and associated high tan δ level render the class uninteresting for practical application.

In the high permittivity systems, the base permittivity itself will always promote dissociation of ionic species either in the compounds themselves, or in associated impurities. Since the transport involves both a carrier concentration and a MOBILITY, the natural attack is then to seek systems of much lower mobility. In this case then it is natural to explore gels where mobility will be orders of magnitude less than the liquid state.

From the dielectric spectrum of the gelatin it appears as a benign host, free from major dielectric features in the radio frequency range. By chemical modification, it does however appear that large dipolar groups can be associated in such a manner that significant orientability is retained and that by choosing different chemistries the relaxation frequency can be moved over more than three orders at room temperature.

The unusual dielectric saturation behavior for the modified gelatins does suggest that there are large associated dipolar clusters. For the triglycine modification, where the relaxation frequency is reasonably fast, the saturation fits quite well a classical Langevin model. In several of the systems however a most unusual enhancement of weak field response appears to occur at higher field levels. For these materials it is tempting to suggest that the slow polarization processes may be speeded up at higher field levels, leading to the observed peaks in response. Much more data is, however, clearly needed to confirm such a hypothesis.

From both Byer-Roundy and Chynoweth results, it is clear that the modified gelatins have most interesting pyroelectric properties under DC bias. At high bias field levels and low chopping frequency the material is clearly superior to $LiTaO_3$ and even for high chopping frequency and low bias the triglycerin-modified gelatin is comparable to the best pyroelectric polymer.

The most puzzling feature of the response in all the modified gelatins is the sharp dielectric peak, reaching very high values at low frequency for temperatures near 30° to 40°C, and the associated double maxima in loss tangent. If the response is dependent upon large associated dipolar clusters, the rapid decay of the polarizability at low frequency suggests that the clusters may be breaking up with increasing temperature. However, the higher temperature maximum in tan δ suggests that any breakup of dipolar clusters must take place in a rather unusual manner so as to produce a slowing down of the polarizability with INCREASING TEMPERATURE.

## 7. SUGGESTIONS FOR FUTURE WORK

The current study was in the nature of a "broad brush" survey of modes by which dielectric properties of "soft dielectrics" in bio-organic systems could be modified and controlled to provide a spectrum of useful properties.

As a result of these studies it does appear that the modified gelatin structures can yield flexible films with pyroelectric properties superior to all other known polymers. However, much more work needs to be done before this promise can be realized.

An obvious shortcoming in the present study is the absence of systematic data for the change of properties as a function of the concentration of polar additive to the gelatin. A second obvious area of need is for more detailed characterization of the mode in which the polar group are incorporated.

Of particular interest are the most unusual sharp peaks in the weak field dielectric permittivity at low frequency, and the associated maxima in the loss. In these studies measurements were made with a slow but continuously moving temperature (usually 3°C/min) and it is not clear that the measured values are necessarily equilibrium properties of the system. Clearly other tools such as IR spectroscopy, differential thermal analysis and differential scanning calorimetry should be applied to check for structural changes near the dielectric maxima.

The preliminary data on bilayer structures do suggest that tan $\delta$ can be significantly reduced without sacrifice of the interesting dielectric response. Present bilayers are a little irregular and it will be necessary to improve methods of fabrication so that systematic studies as a function of the thickness of the two components can be accomplished and the results then fully analyzed using composite theory.

As the properties of the host proteins are improved it will become most interesting to explore composites which include very fine scale suspensions of high permittivity inorganic ferroelectrics. The MRL has a DARPA sponsored program on Ferroic Nanocomposites which can supply just the types of powders needed for these studies.

A property of the gelatin which has not been exploited so far is its viscoelastic behavior which could be used to impart handedness (chirality) to these gelatin based compounds and composites.

From the clear evidence of strong pyroelectric response, it is evident that the modified gelatin films must also be piezoelectric, however because of viscoelasticity at room temperature it will be difficult to measure by traditional resonance methods. For initial studies we would propose to explore the response under nonresonant conditions by using the MRL's AC ultradilatometer which is capable of measuring AC strains down to $10^{-3}$ Å.

If the piezoelectric response is interesting it may then be worthwhile to concentrate some efforts upon stiffening the structure for resonant applications.

The pyroelectric and piezoelectric responses indicate that the poled gelatins should also have non-zero linear electrooptic and nonlinear (SHG) coefficients. As the optical quality of the gelatin systems is improved, it will be important to explore these optical responses.

#3: KDHFM4

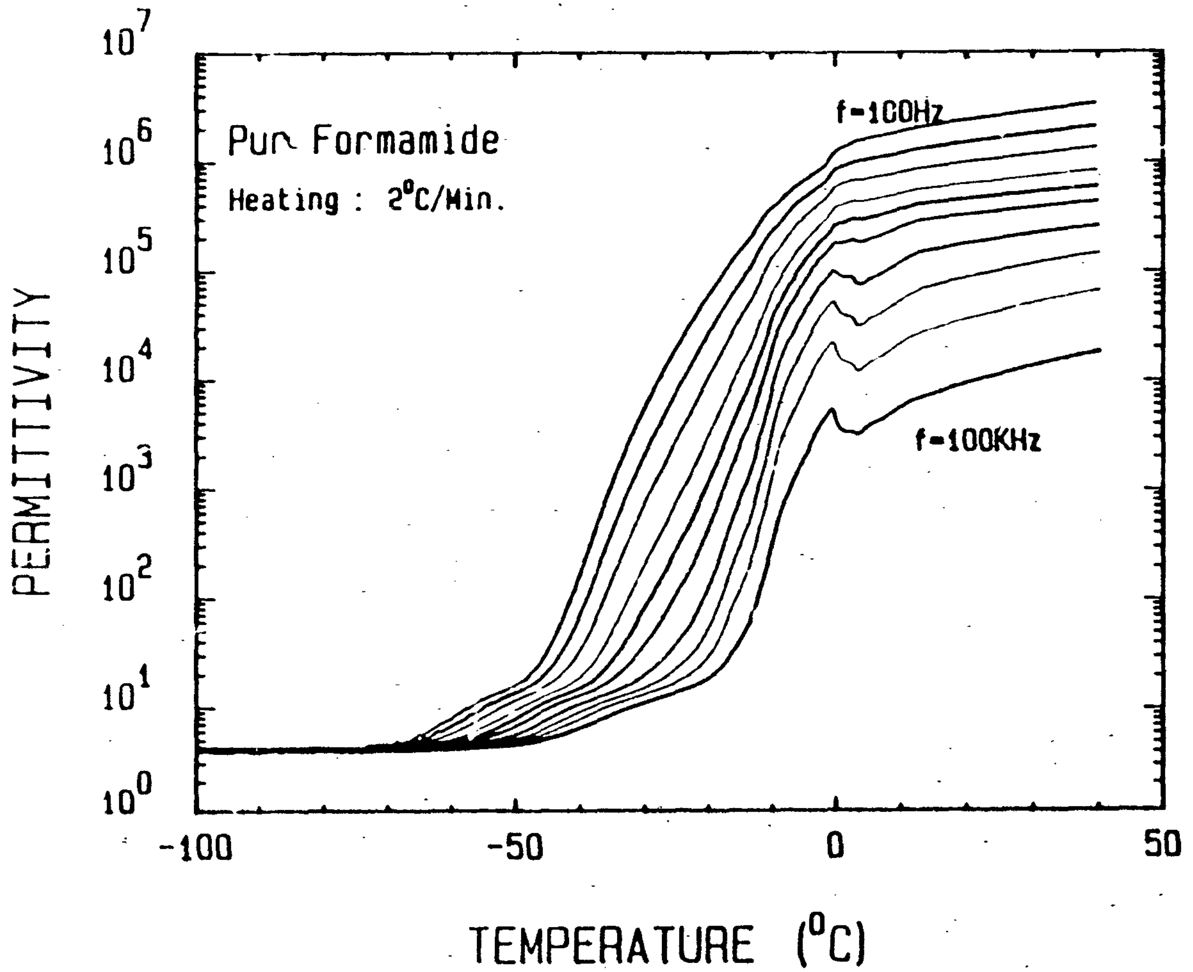


Fig. 1(a)

#3: KDHFM4

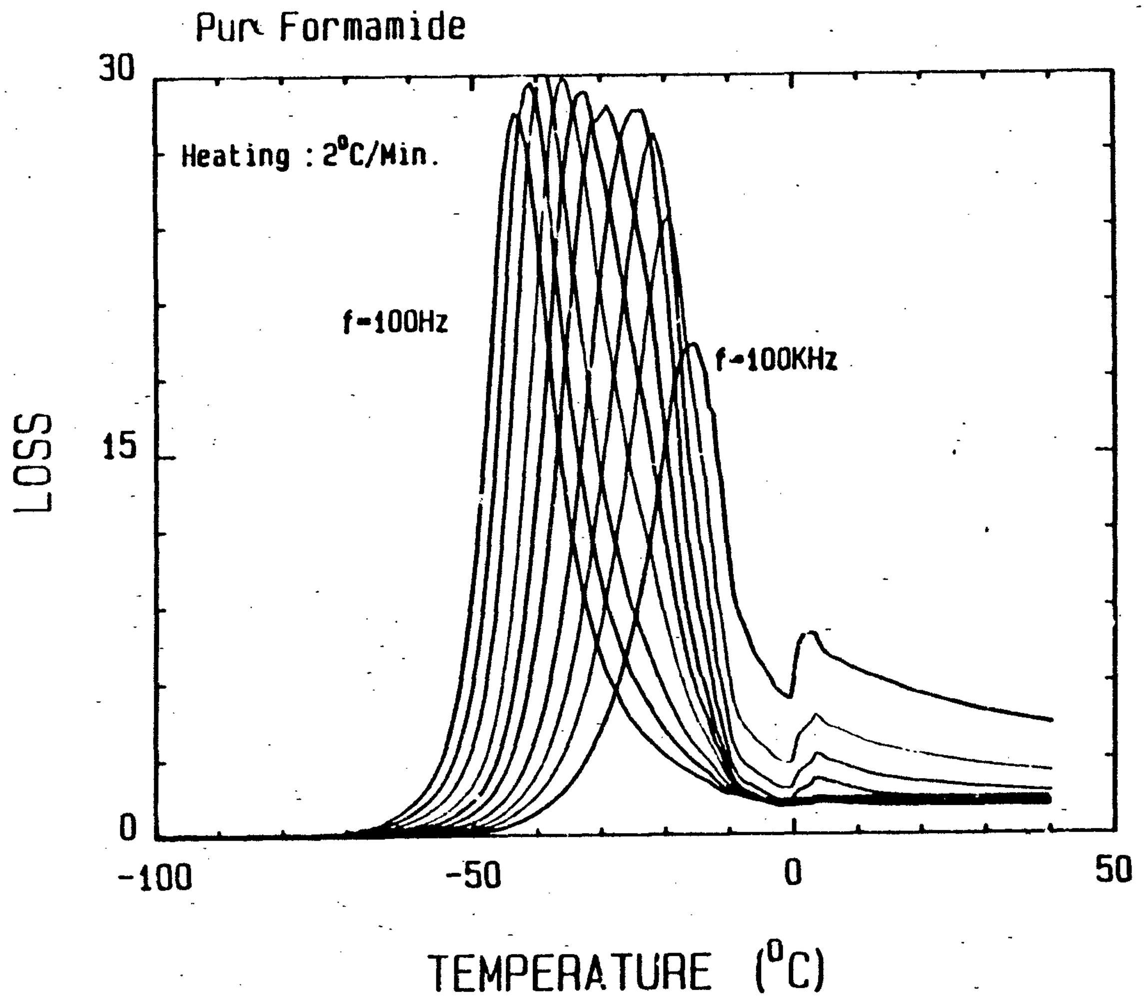


fig 1(b)

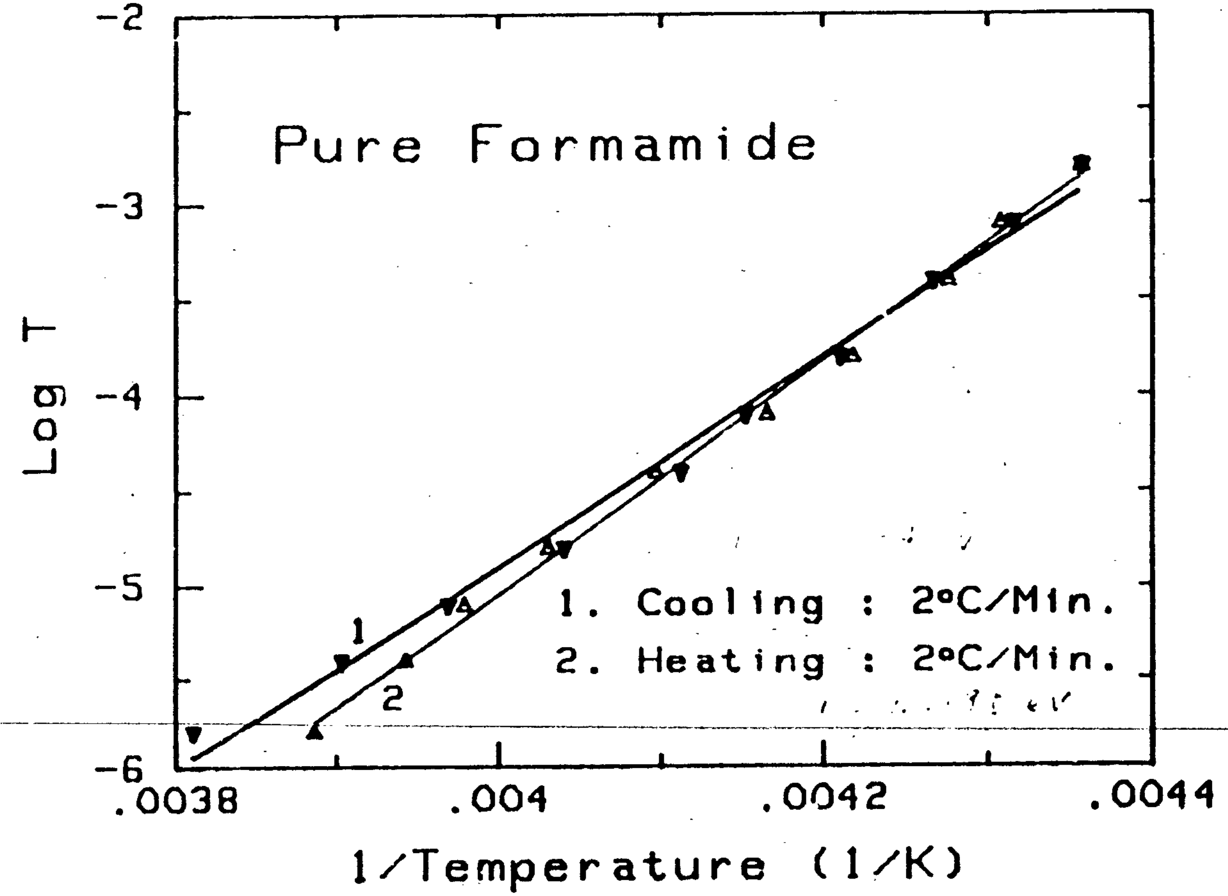

Pure Formamide
Log T
-2
-3
-4
-5
-6
.0038
.004
.0042
.0044
1/Temperature (1/K)
1
2
1. Cooling : 2°C/Min.
2. Heating : 2°C/Min.

fig 2

#3: KDCFM5

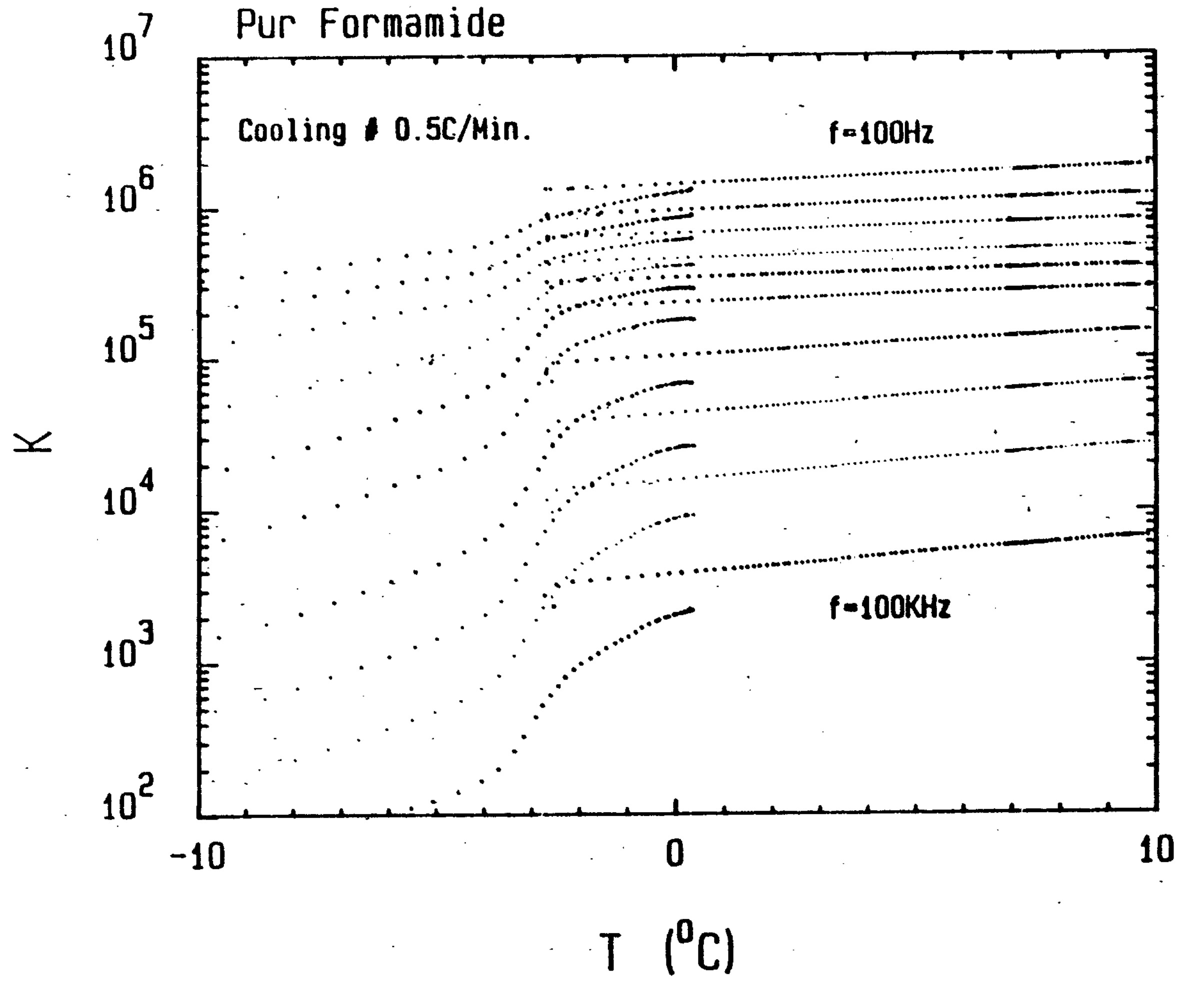


fig 3(a)

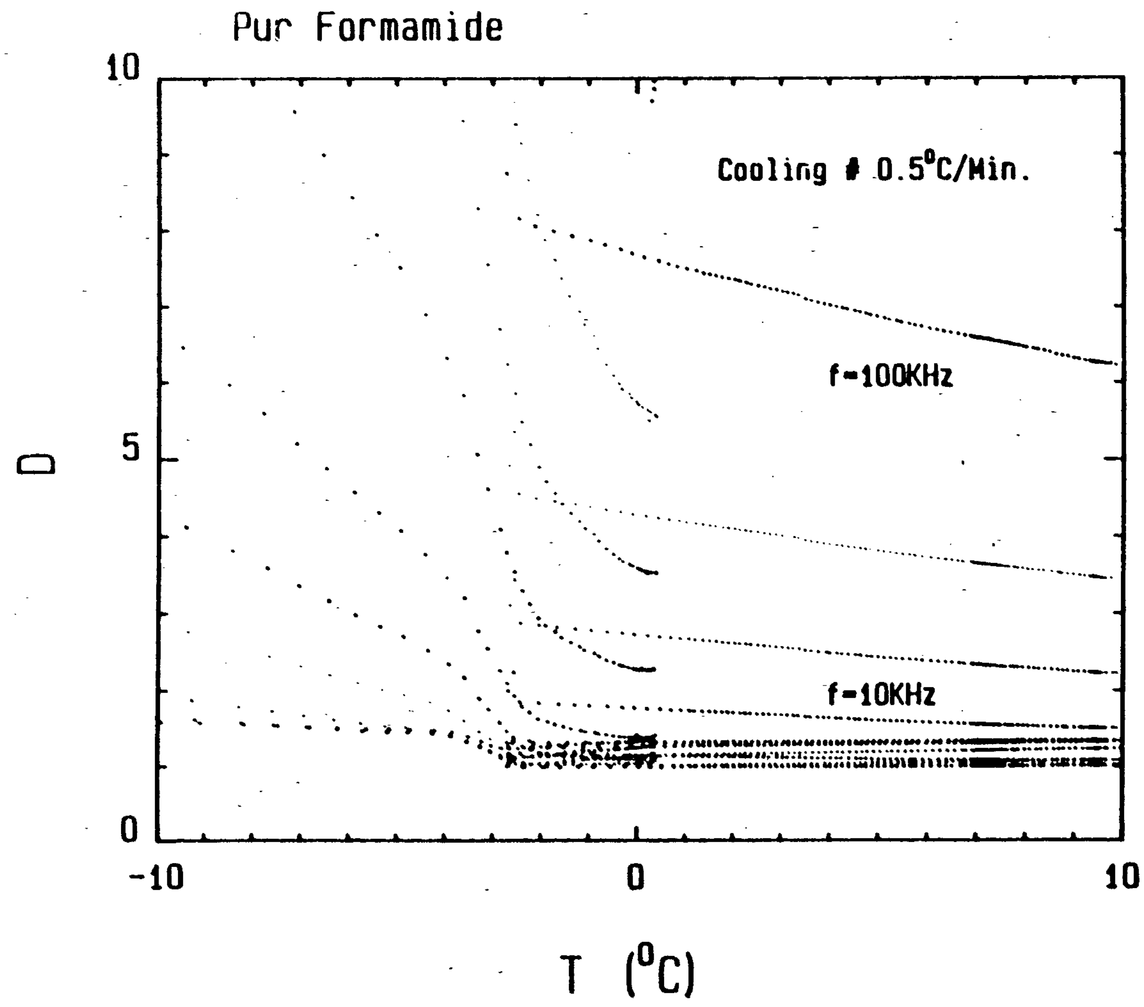

Pur Formamide
Cooling # 0.5°C/Min.
f=100KHz
f=10KHz
D
10
5
0
-10
0
10
T (°C)

Fig 3 (b).

July 29_87
#3: KOCMFM3

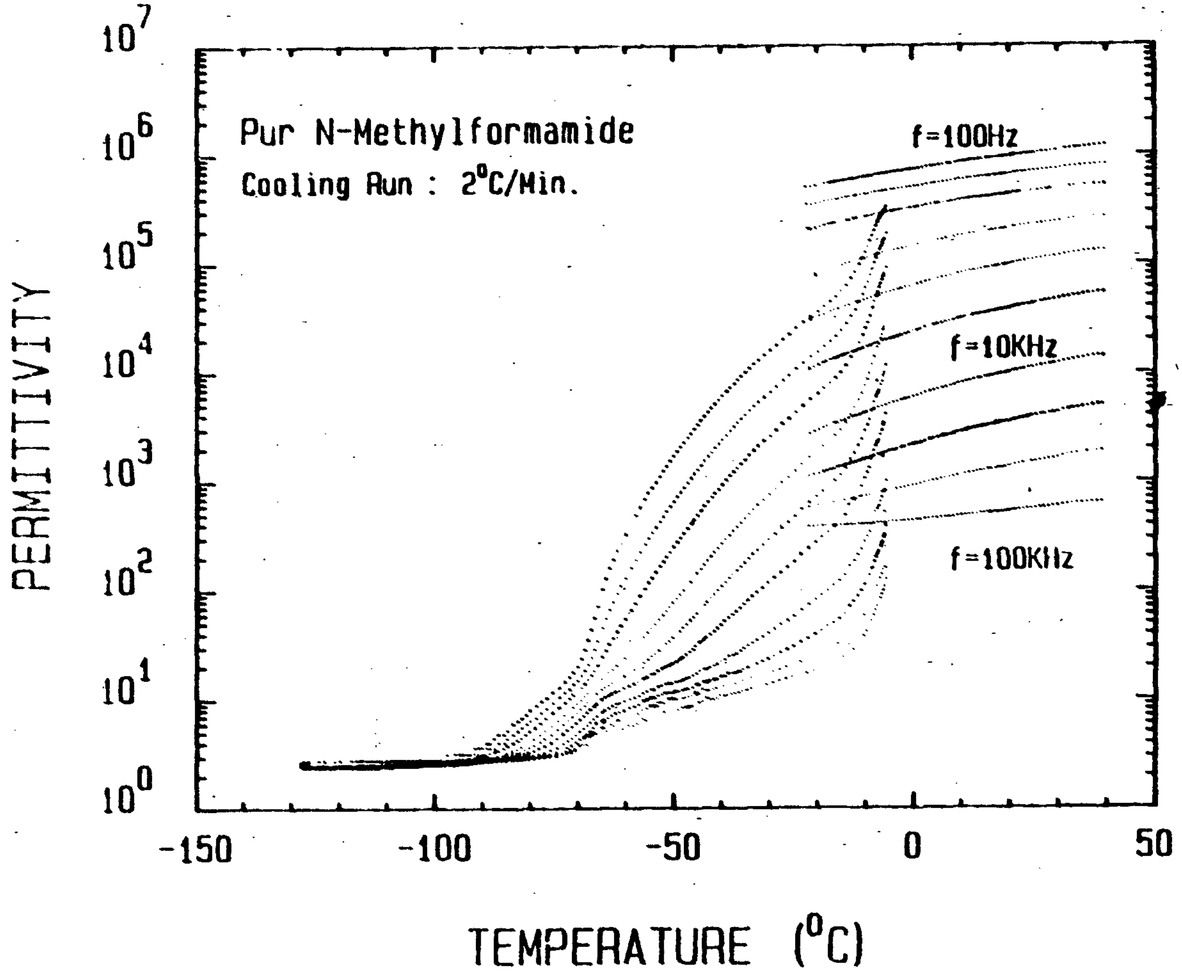


Fig 4(a),

#3: KOCMFM3

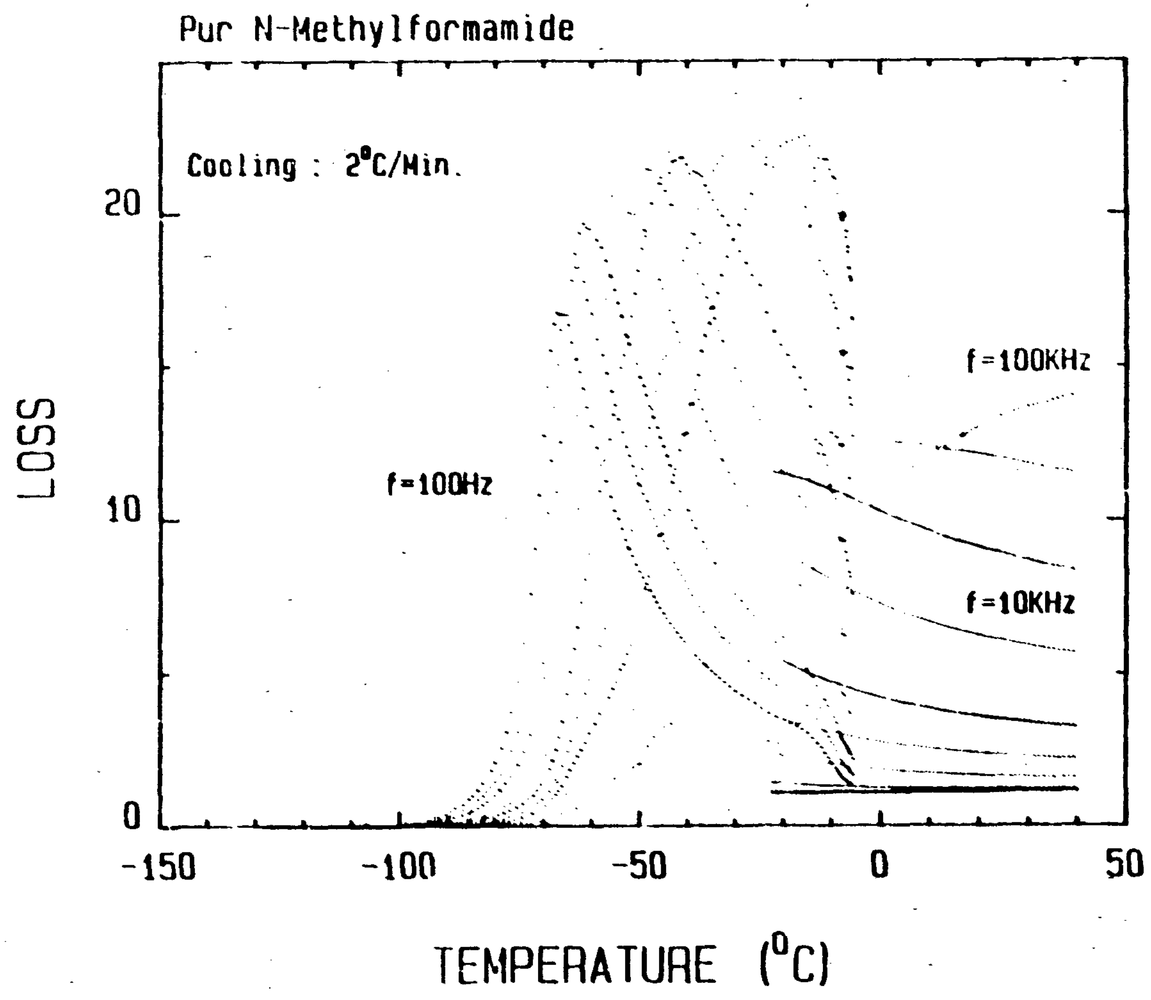


Fig 4(b)

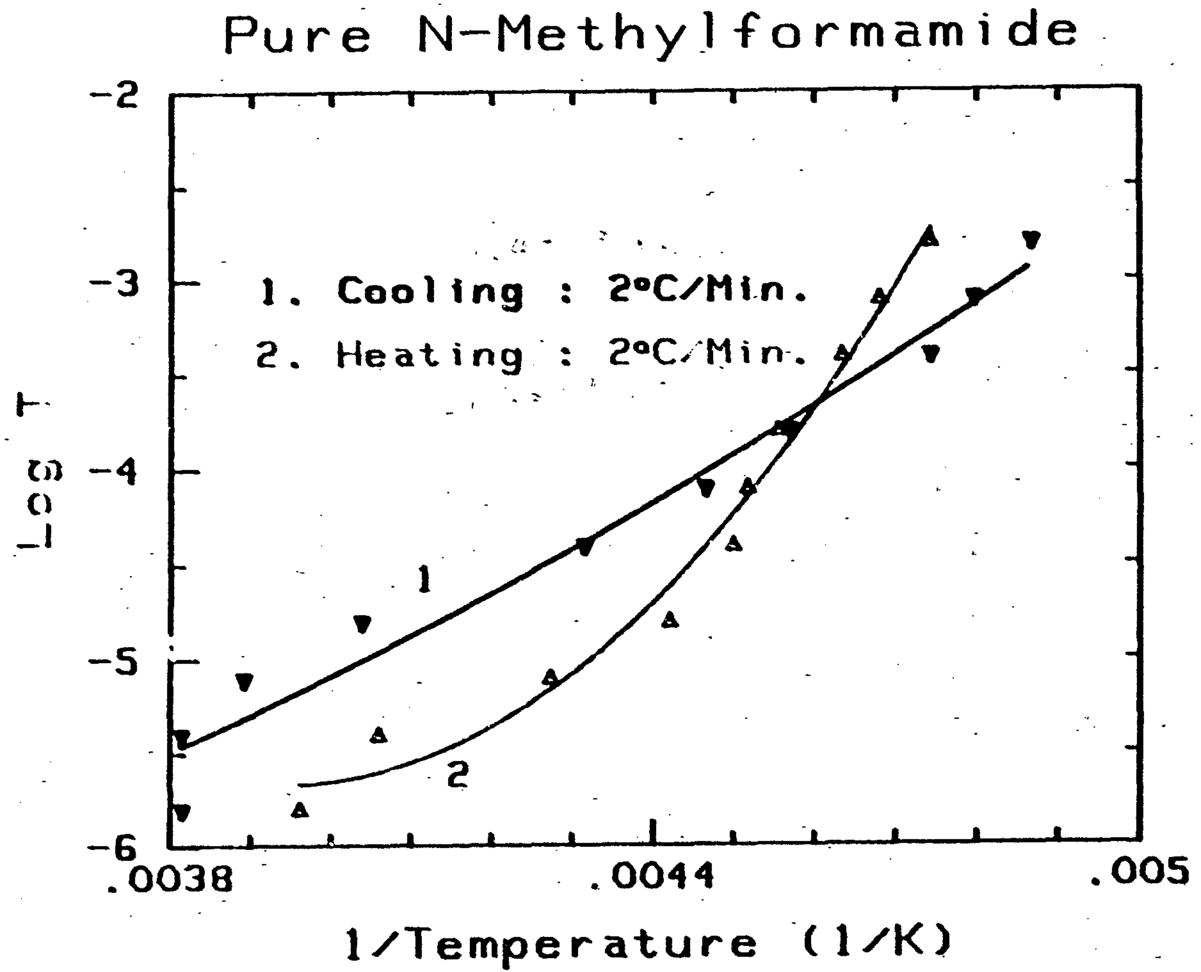

Pure N-Methylformamide
1. Cooling : 2°C/Min.
2. Heating : 2°C/Min.
1
2
Log T
-2
-3
-4
-5
-6
.0038
.0044
.005
1/Temperature (1/K)

Fig 5

#3 KJHDMFM3

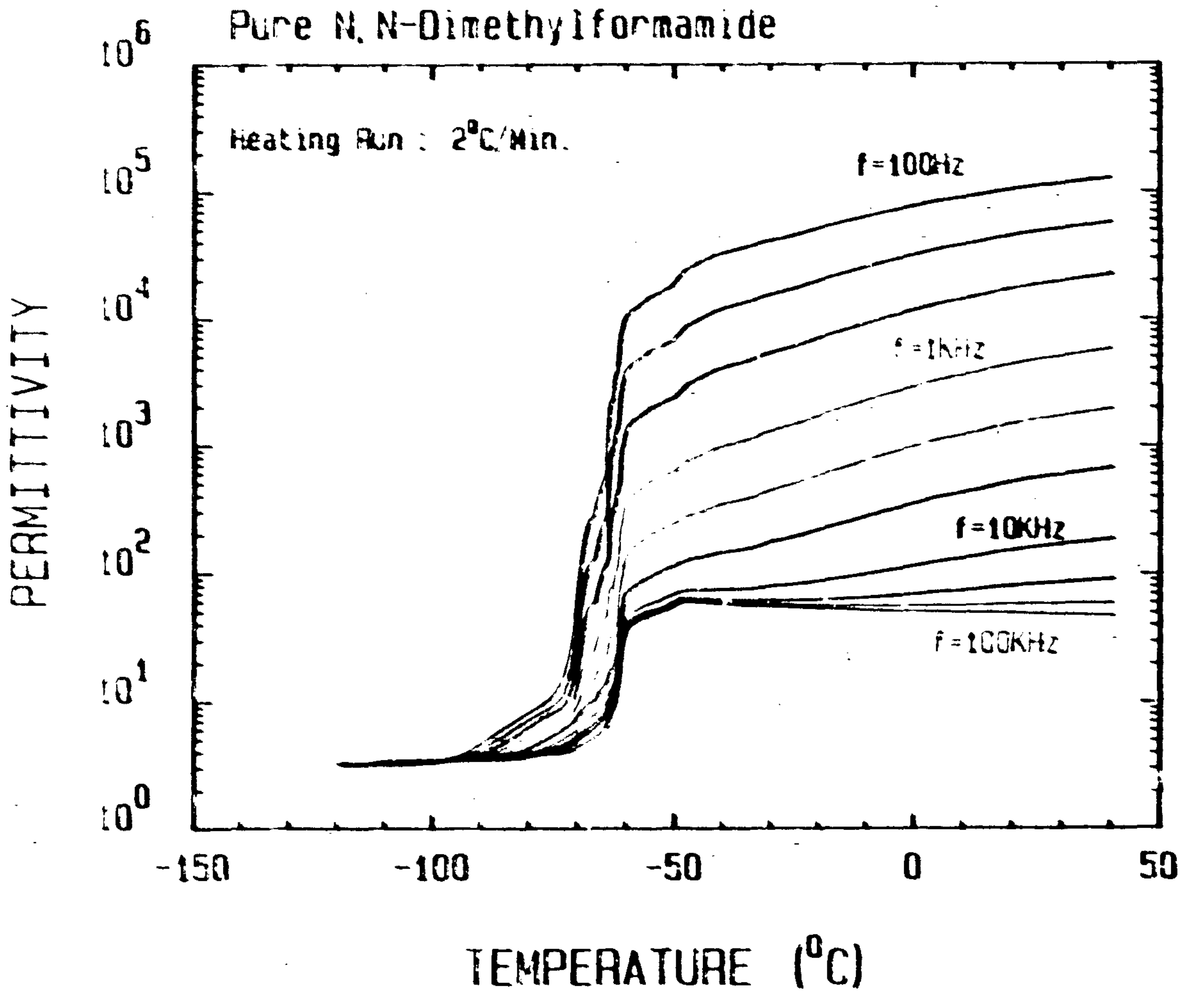


Fig 6(a)

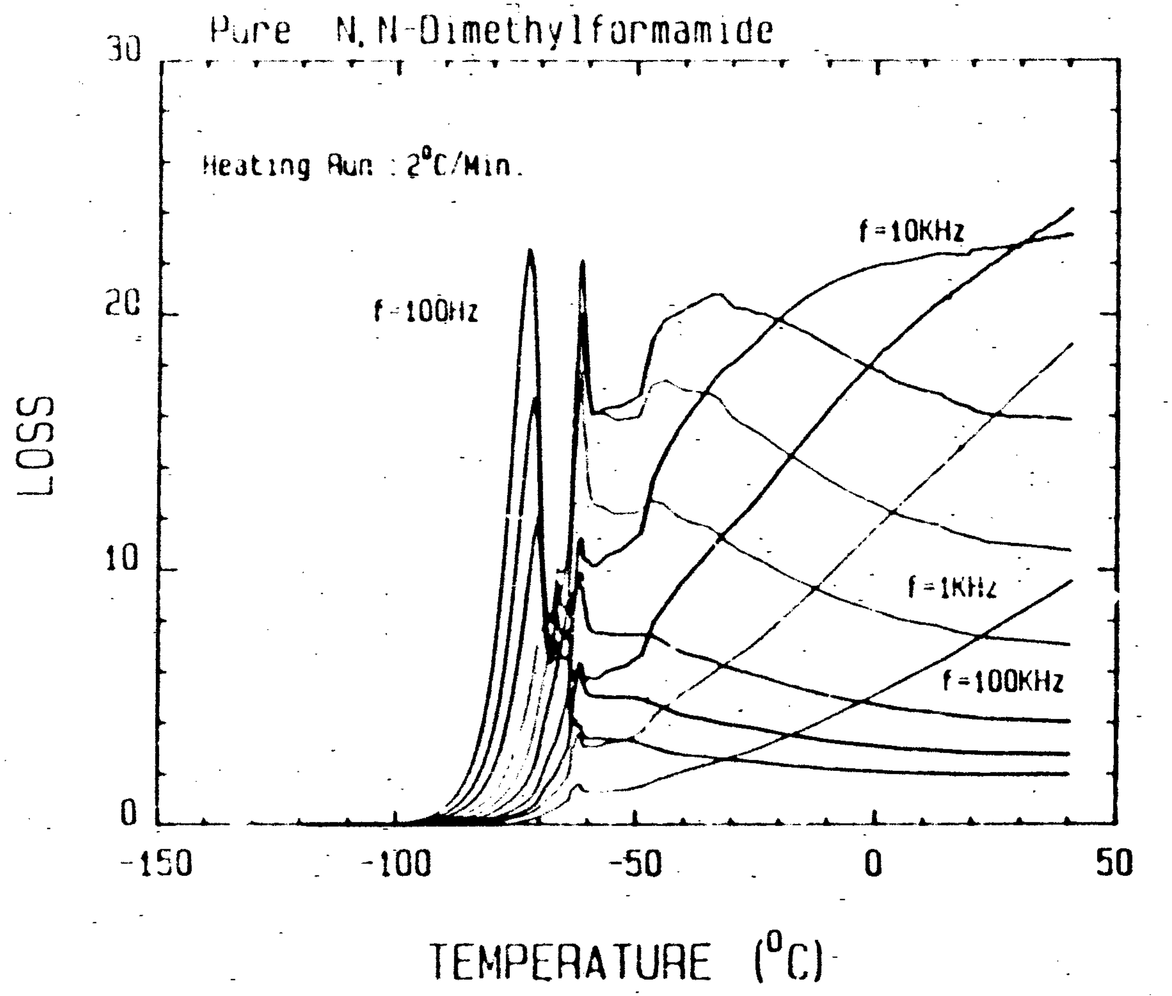

Pure N,N-Dimethylformamide
Heating Run : 2°C/Min.
f = 100Hz
f = 10KHz
f = 1KHz
f = 100KHz
LOSS
0
10
20
30
-150
-100
-50
0
50
TEMPERATURE (°C)

Fig 6(b)

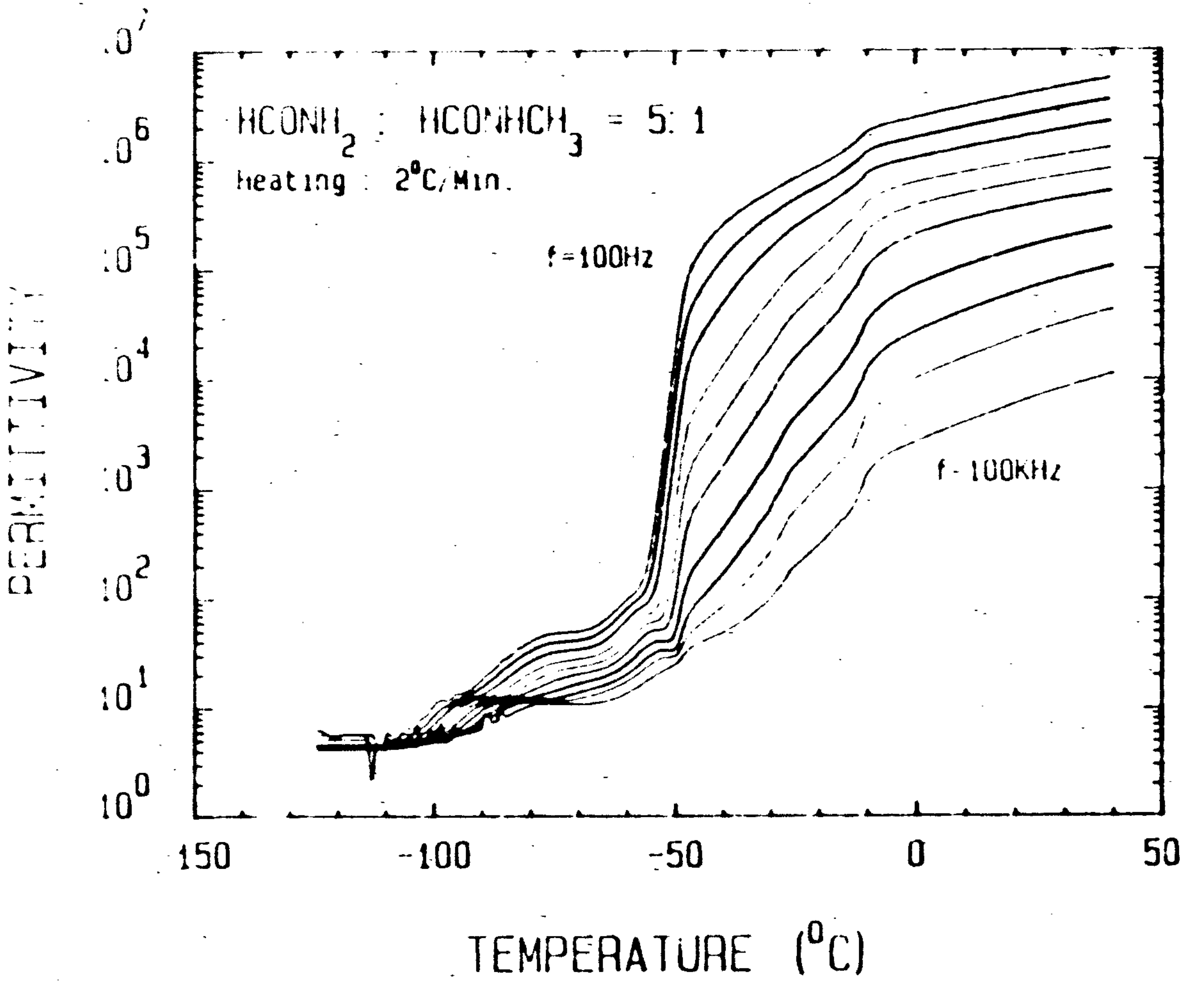

HCONH$_2$ : HCONHCH$_3$ = 5: 1
Heating : 2°C/Min.
f=100Hz
f-100KHz
PERMITTIVITY
$10^7$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
150
-100
-50
0
50
TEMPERATURE (°C)

Fig 7(a)

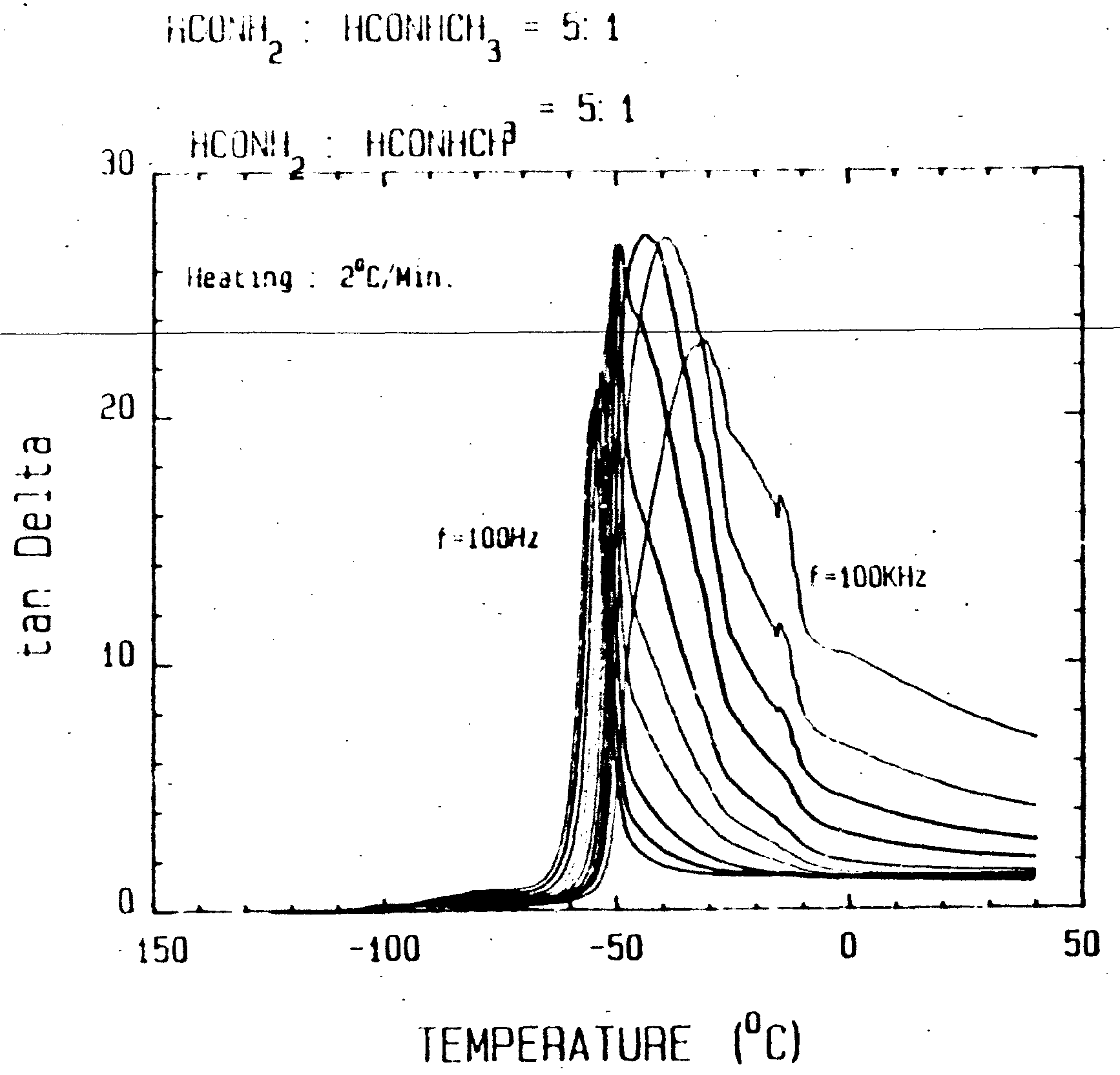

HCONH2 : HCONHCH3 = 5: 1
HCONH2 : HCONHCH3 = 5: 1
Heating : 2°C/Min.
f=100Hz
f=100KHz
tan Delta
30
20
10
0
150
-100
-50
0
50
TEMPERATURE (°C)

Fig 7(b)

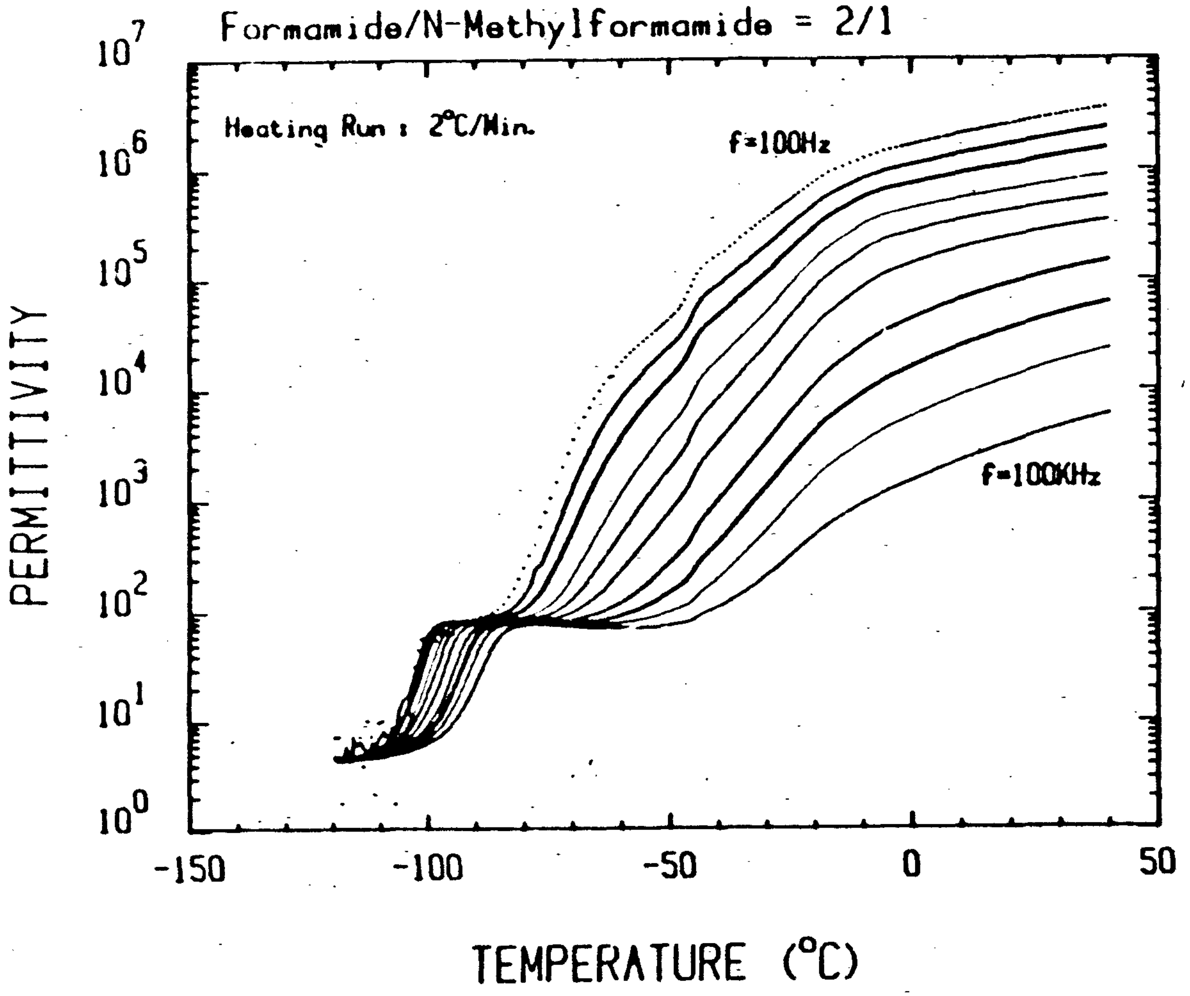

Formamide/N-Methylformamide = 2/1
Heating Run : 2°C/Min.
f=100Hz
f=100KHz
PERMITTIVITY
$10^7$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
-150
-100
-50
0
50
TEMPERATURE (°C)

Fig 8(a)

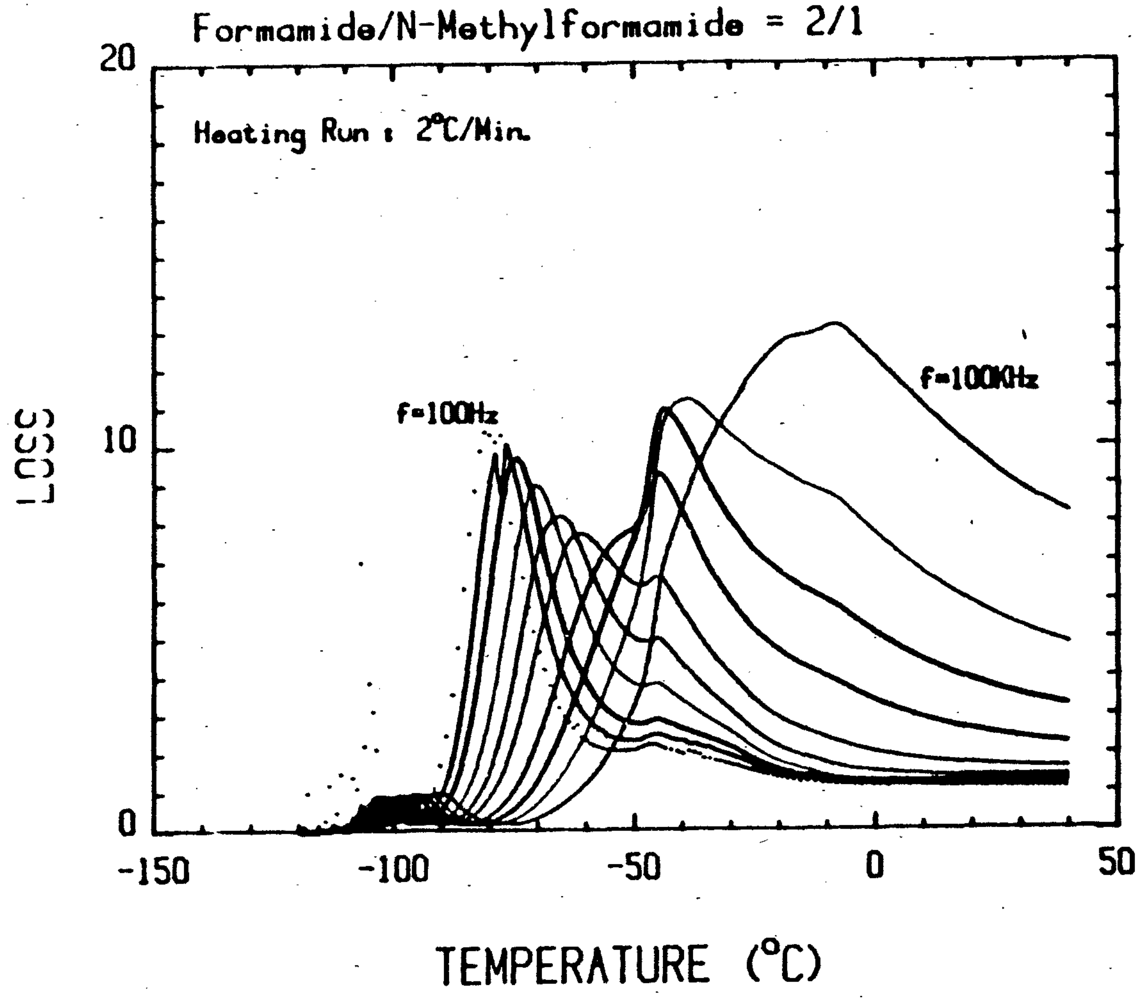

Formamide/N-Methylformamide = 2/1
Heating Run : 2°C/Min.
f=100Hz
f=100KHz
LOSS
20
10
0
-150
-100
-50
0
50
TEMPERATURE (°C)

Fig 8(b)

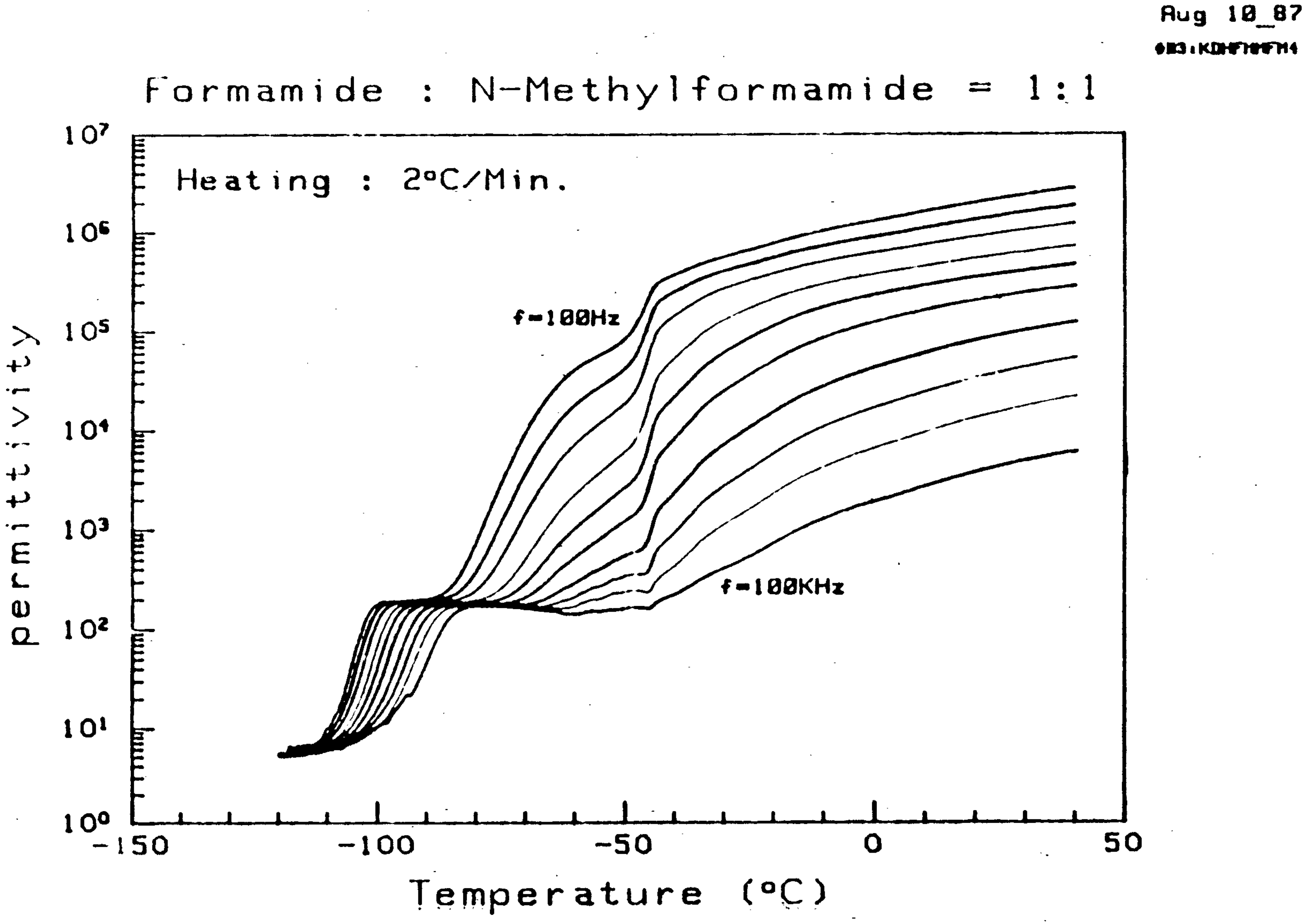
Aug 10_87
Formamide : N-Methylformamide = 1:1
Heating : 2°C/Min.
f=100Hz
f=100KHz
permittivity
10⁰
10¹
10²
10³
10⁴
10⁵
10⁶
10⁷
-150
-100
-50
0
50
Temperature (°C)

Fig 9(a).

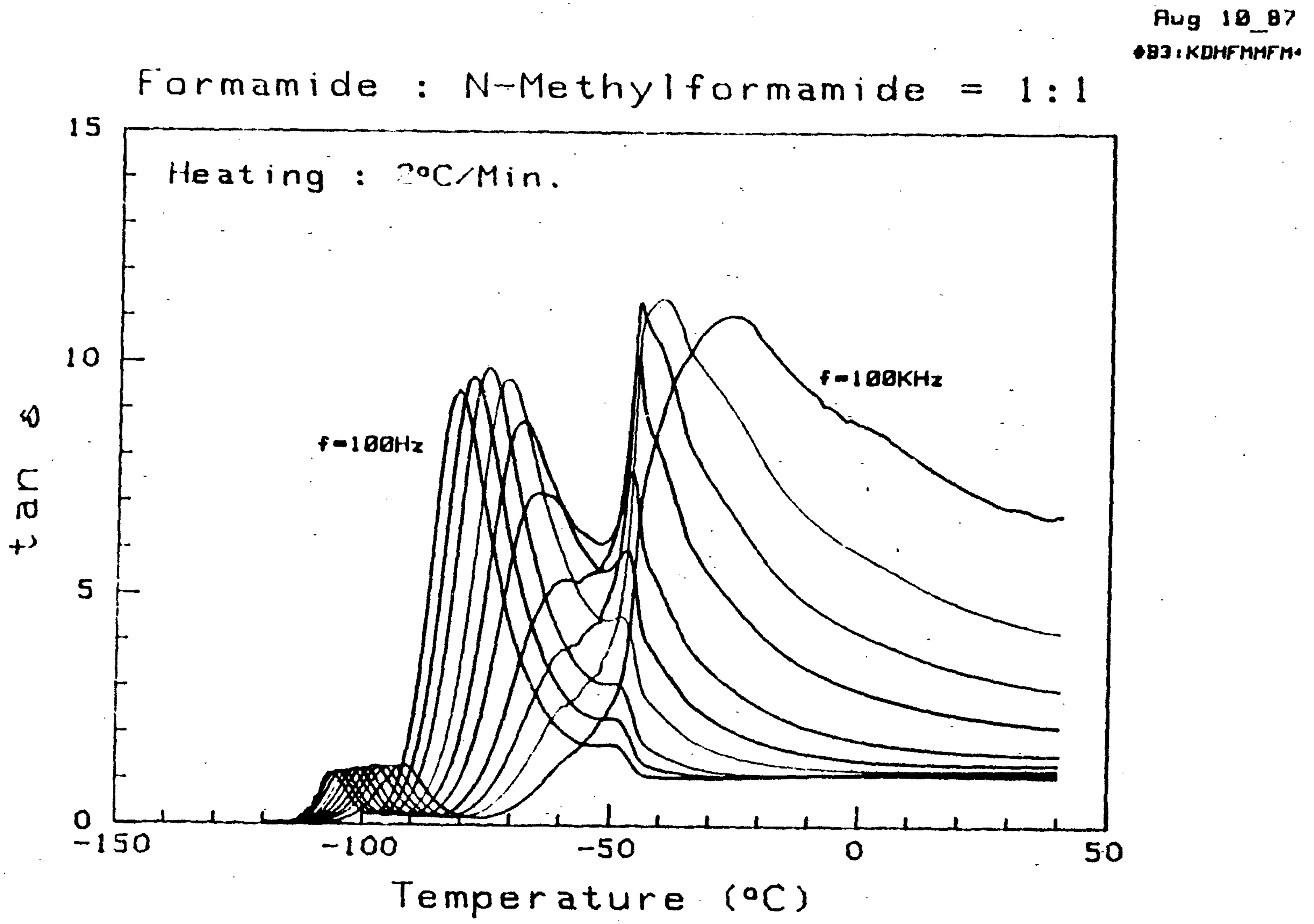

Aug 10_87
#B3:KDHFMMFM•
Formamide : N-Methylformamide = 1:1
Heating : 2°C/Min.
f=100Hz
f=100KHz
tan δ
15
10
5
0
-150
-100
-50
0
50
Temperature (°C)

Fig9(b)

#B3: KDHFMMFM3

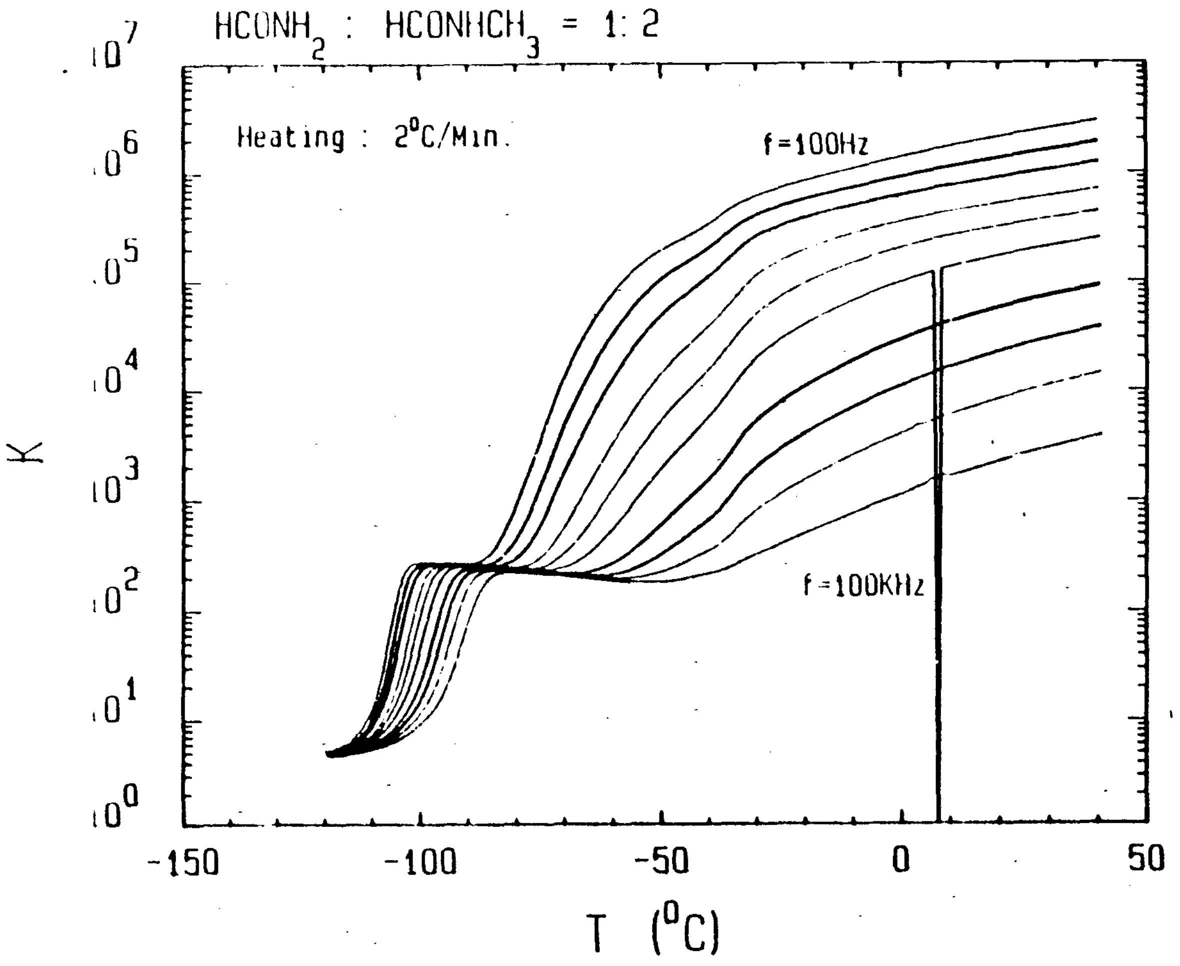


Fig 10(a)

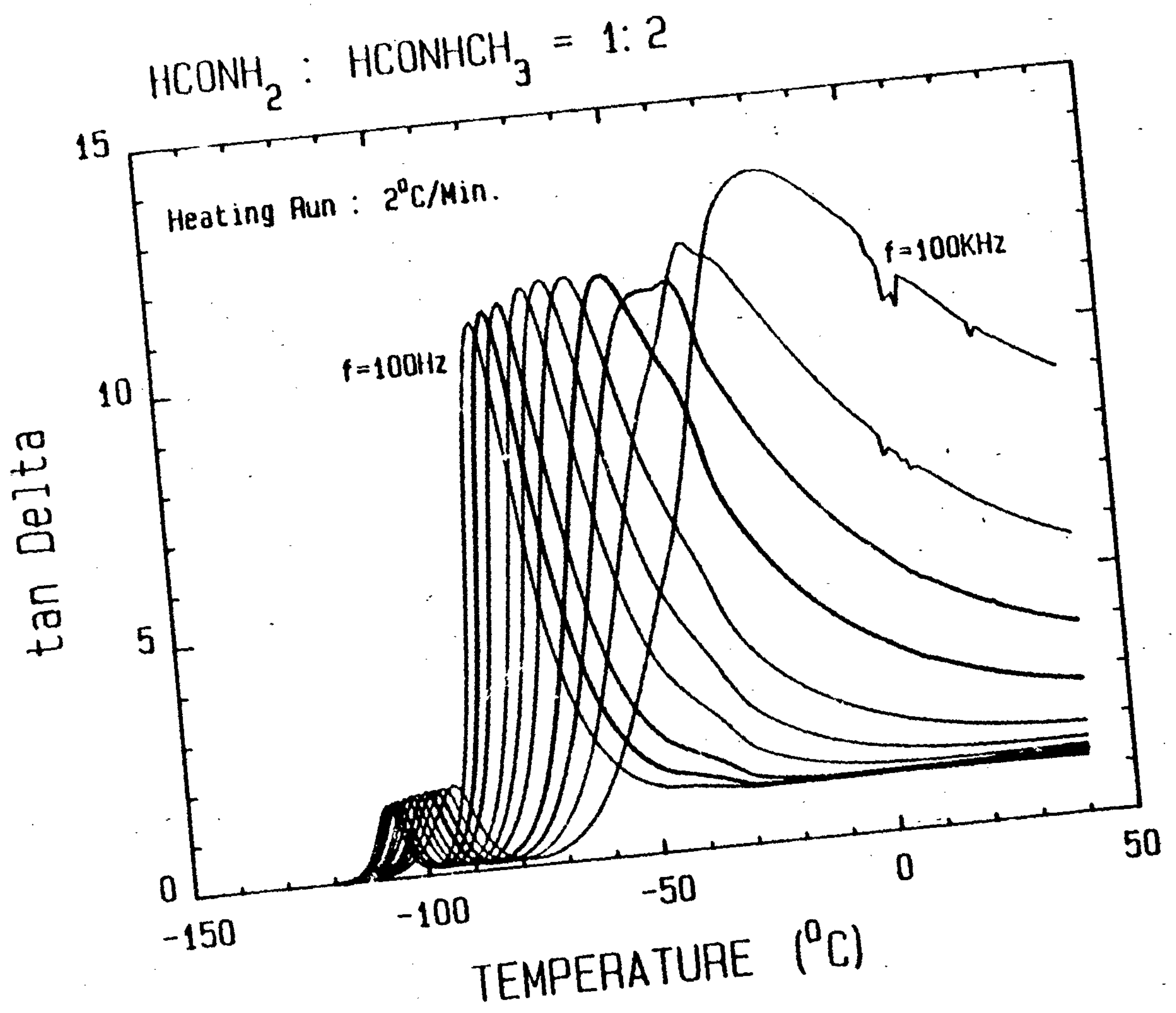

HCONH$_2$ : HCONHCH$_3$ = 1: 2
Heating Run : 2$^0$C/Min.
f=100Hz
f=100KHz
tan Delta
15
10
5
0
-150
-100
-50
0
50
TEMPERATURE ($^0$C)

Fig.10(b)

Aug 12_87
◆B3:KDHFMDMFM1

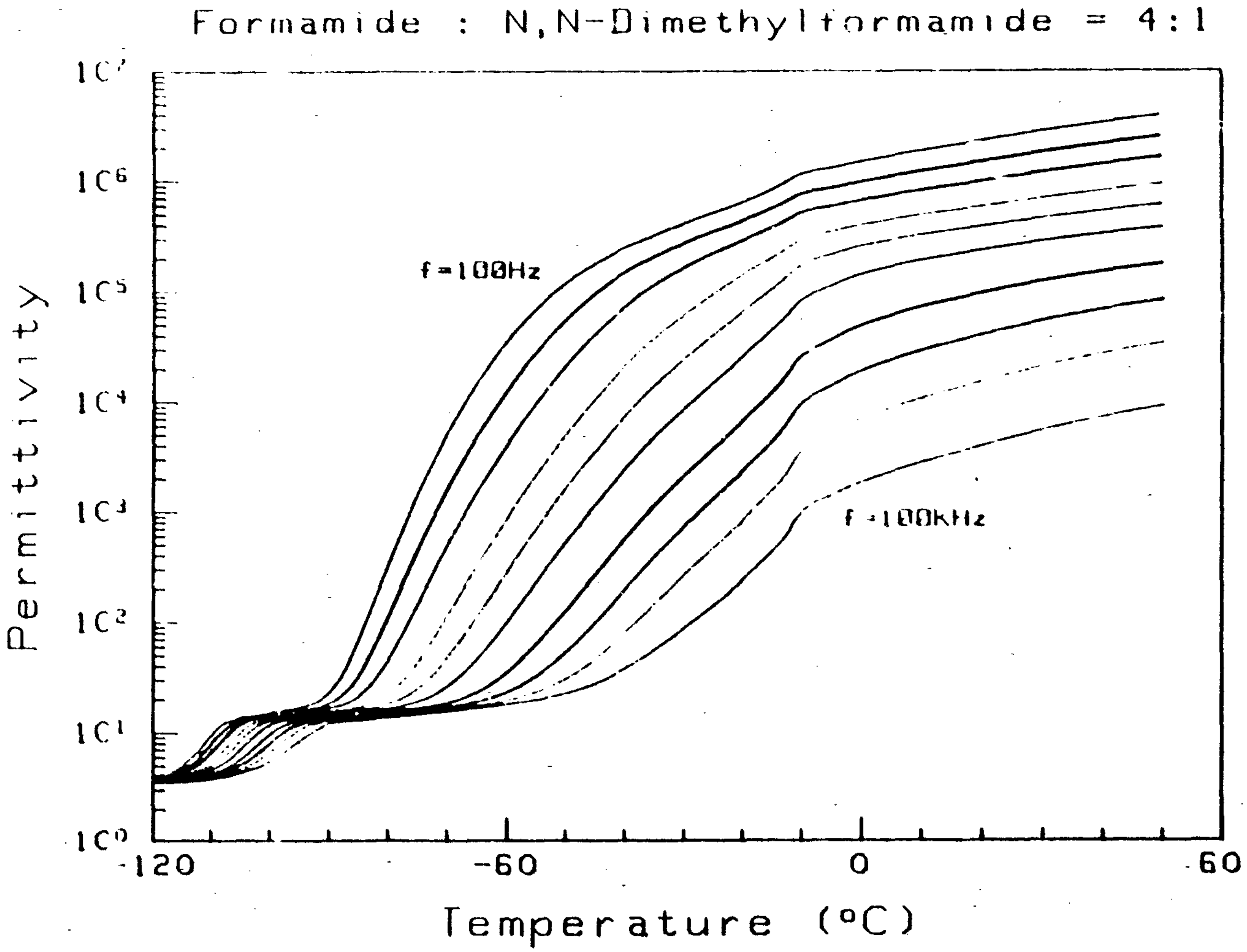


Fig 11(a)

Aug 12_87
#B3:KDMFMDMFM1

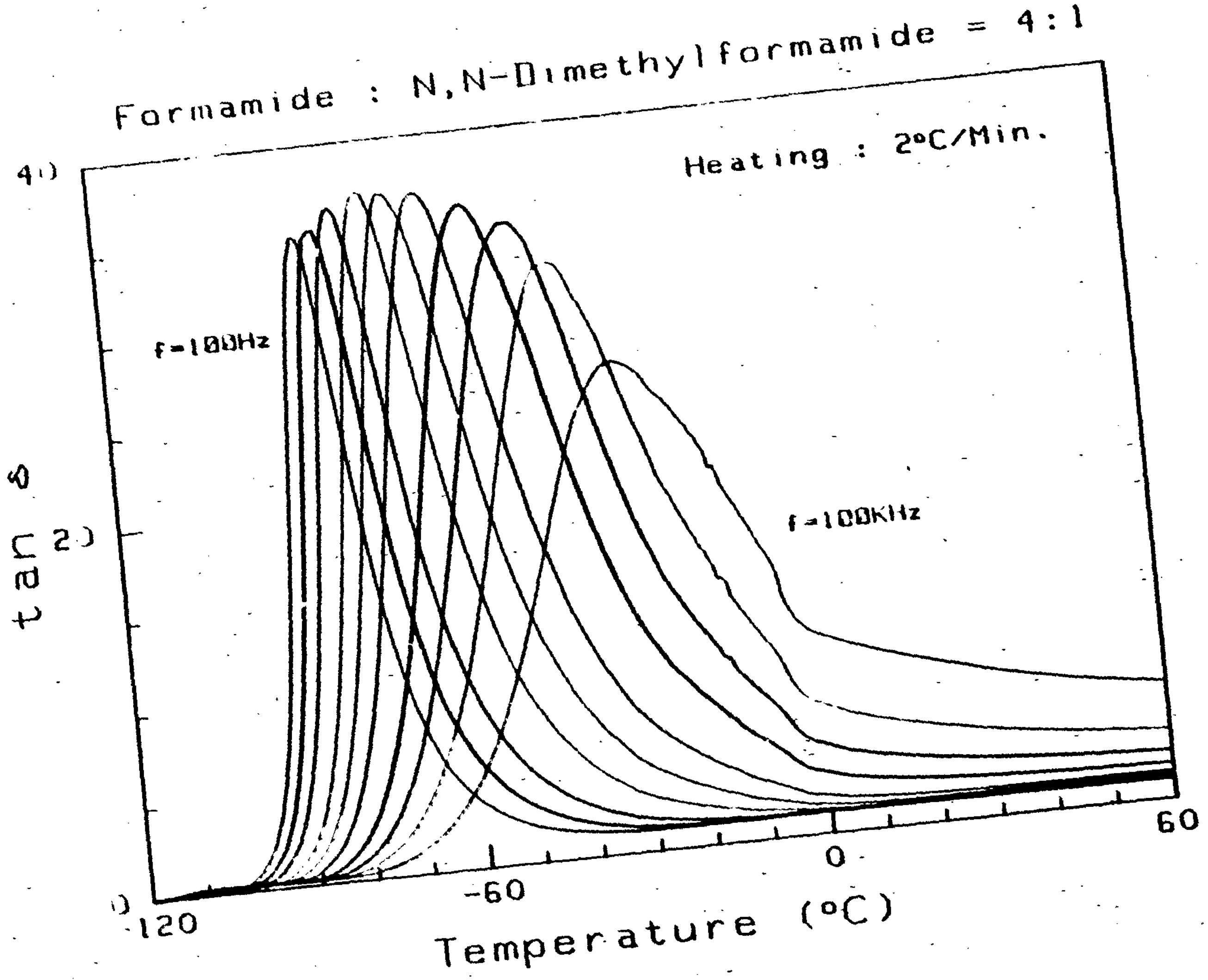


Fig 11(b)

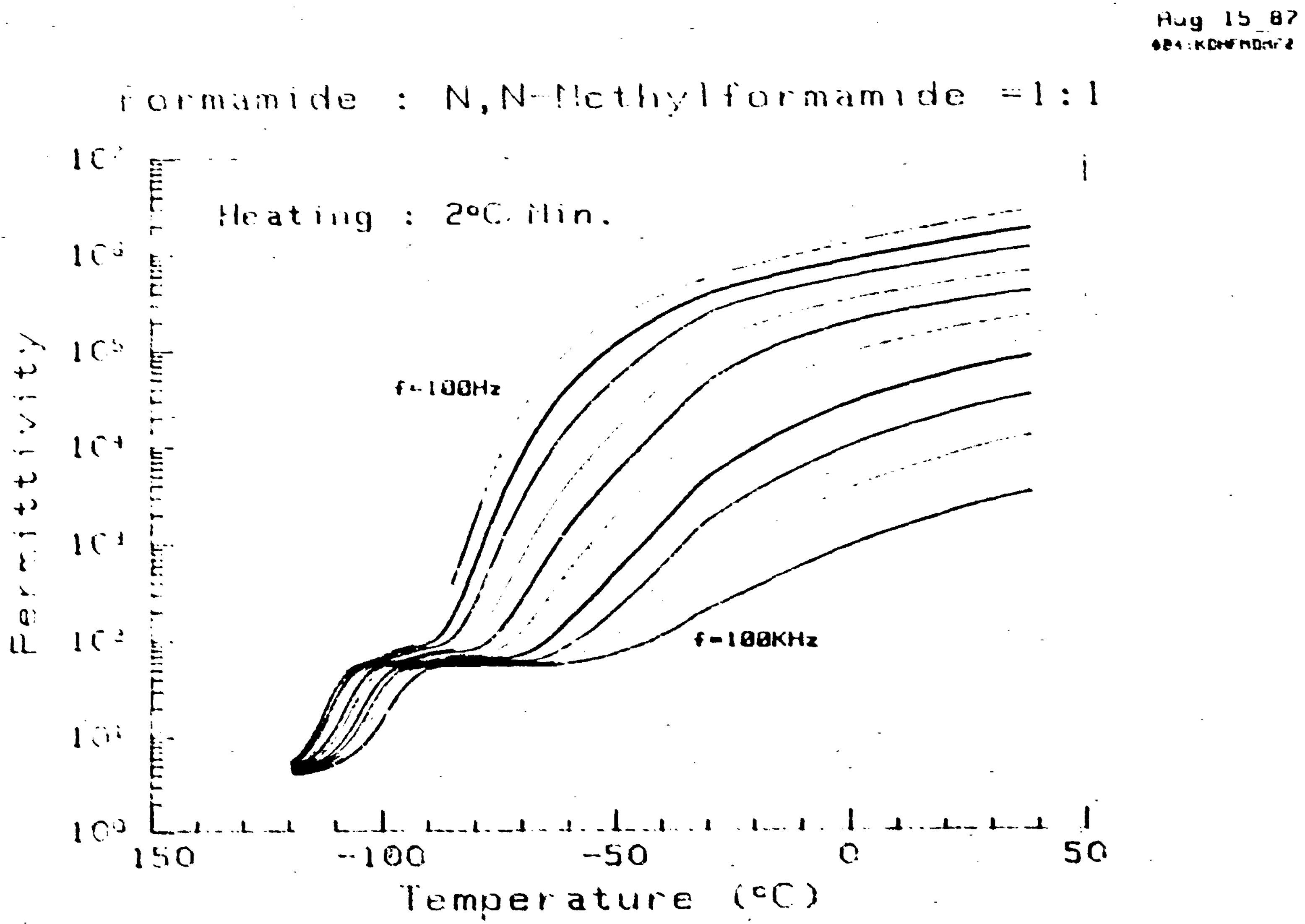

Aug 15_87
Formamide : N,N-Methylformamide =1:1
Heating : 2°C Min.
f=100Hz
f=100KHz
Permittivity
$10^7$
$10^6$
$10^5$
$10^4$
$10^3$
$10^2$
$10^1$
$10^0$
150
-100
-50
0
50
Temperature (°C)

Fig12(a)

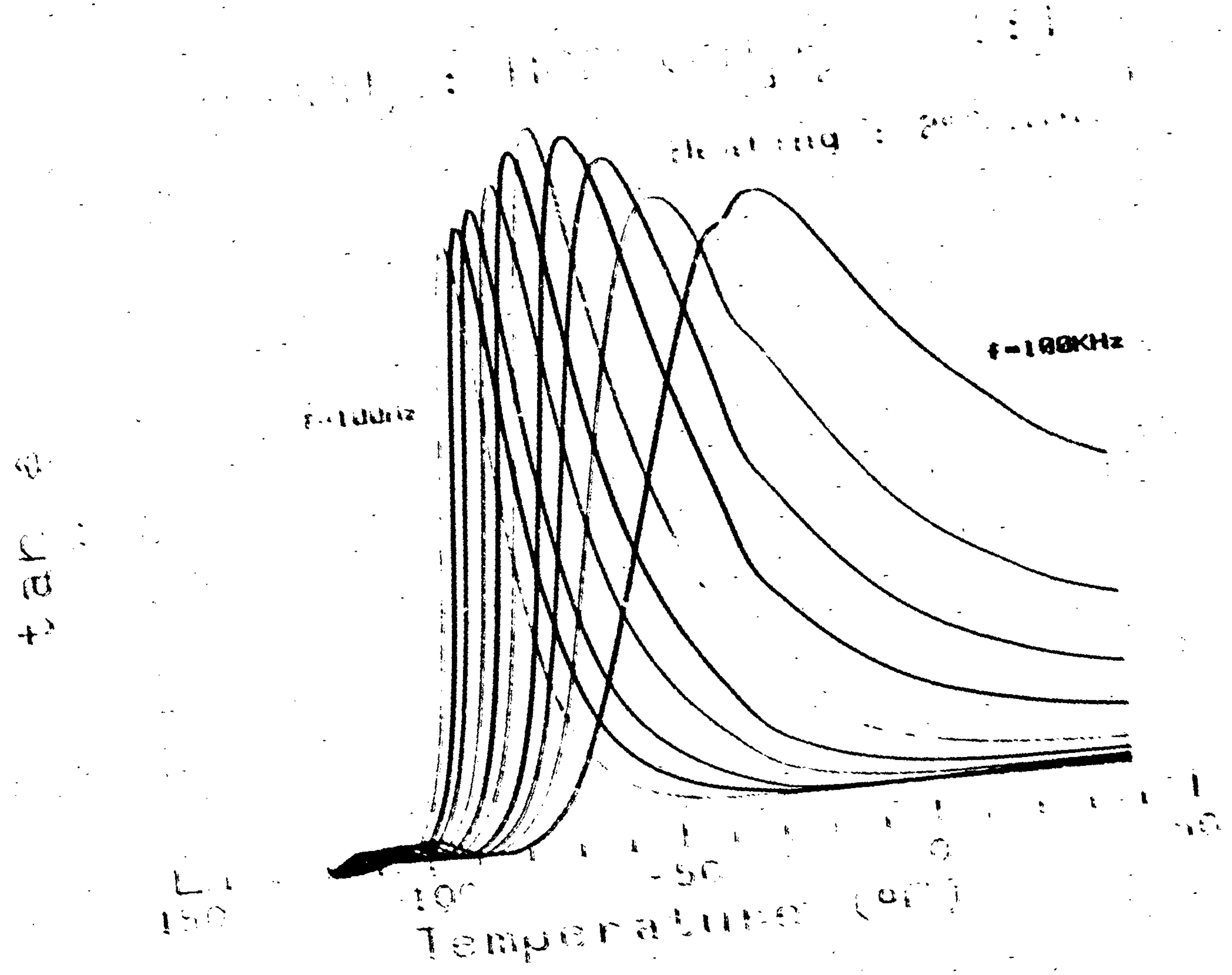


Fig 12(b)

Aug 27_87
084:KDCPMZ_3

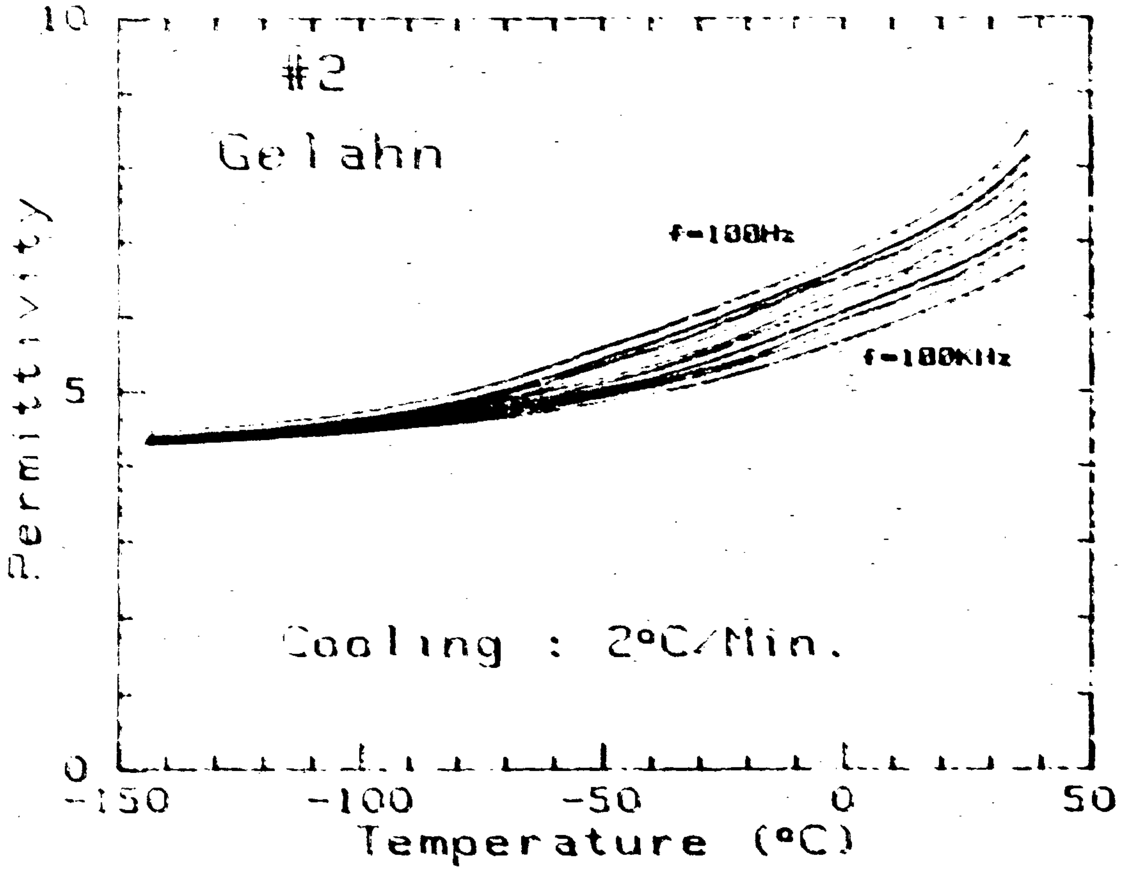


Fig 13(a)

Aug 27 87
0B4:KDCPM2_3

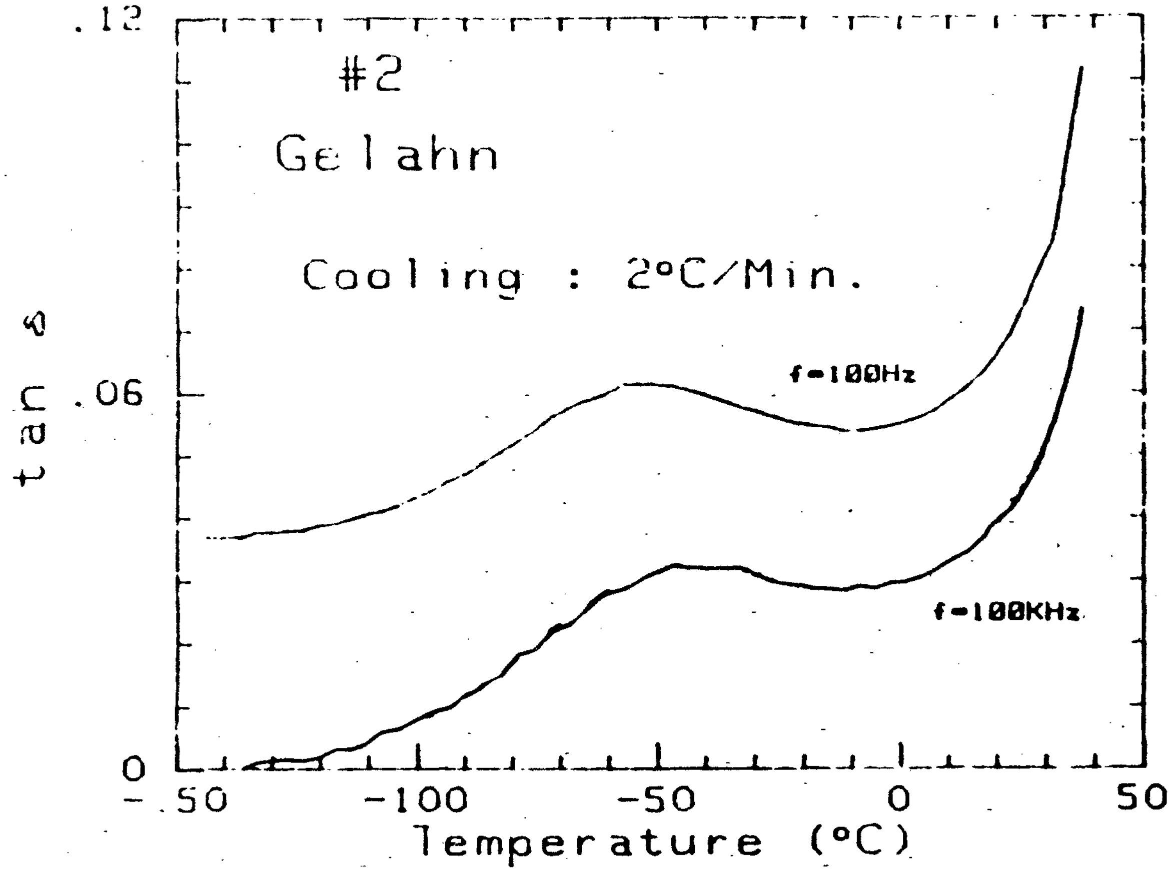
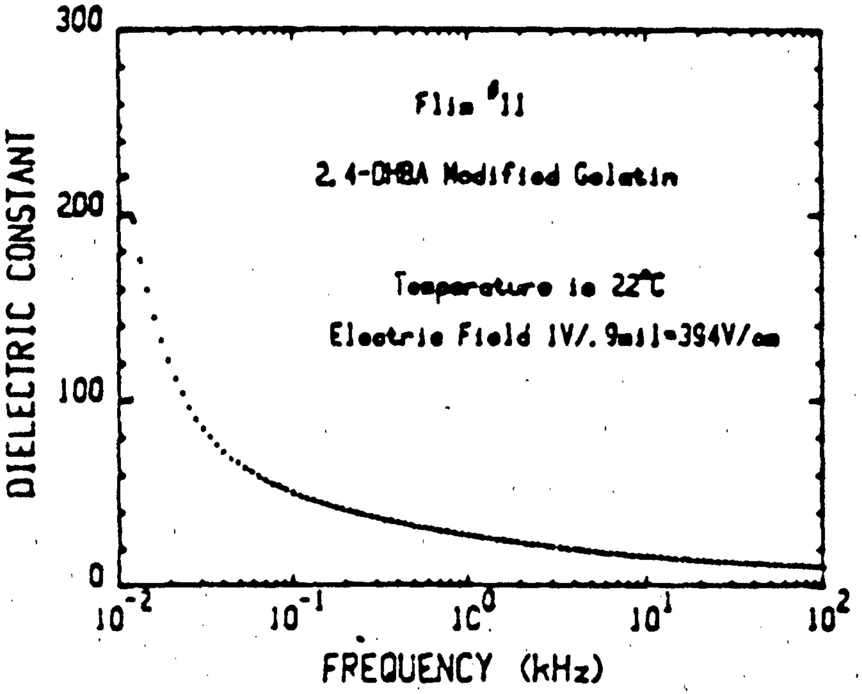
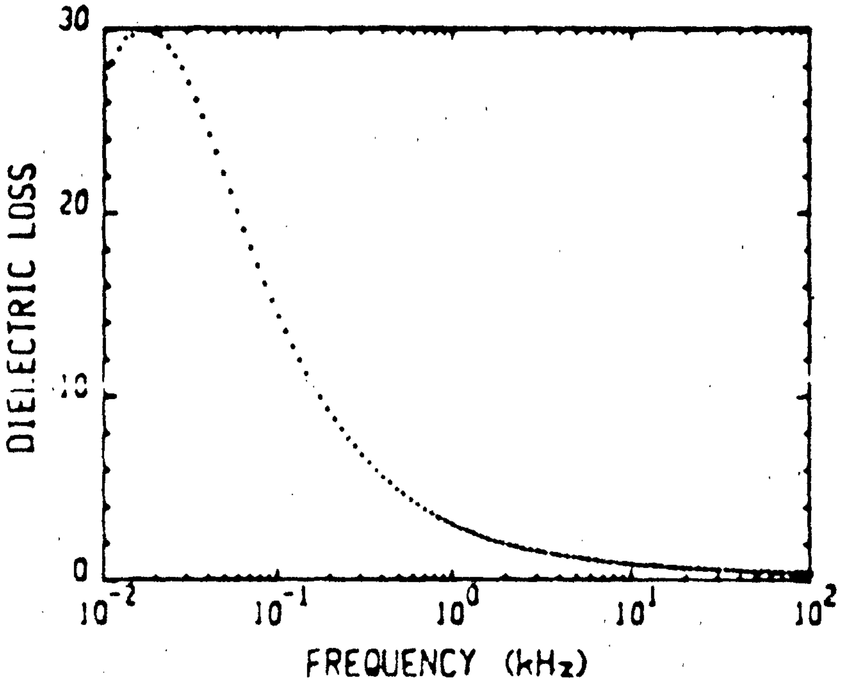


Fig 13(b)



Dielectric constant vs log frequency
2,4 DHBA modified gelatin at 22°C 394 V/cm.

Fig
14(a).



Dielectric loss vs log frequency.

Fig
14(b)

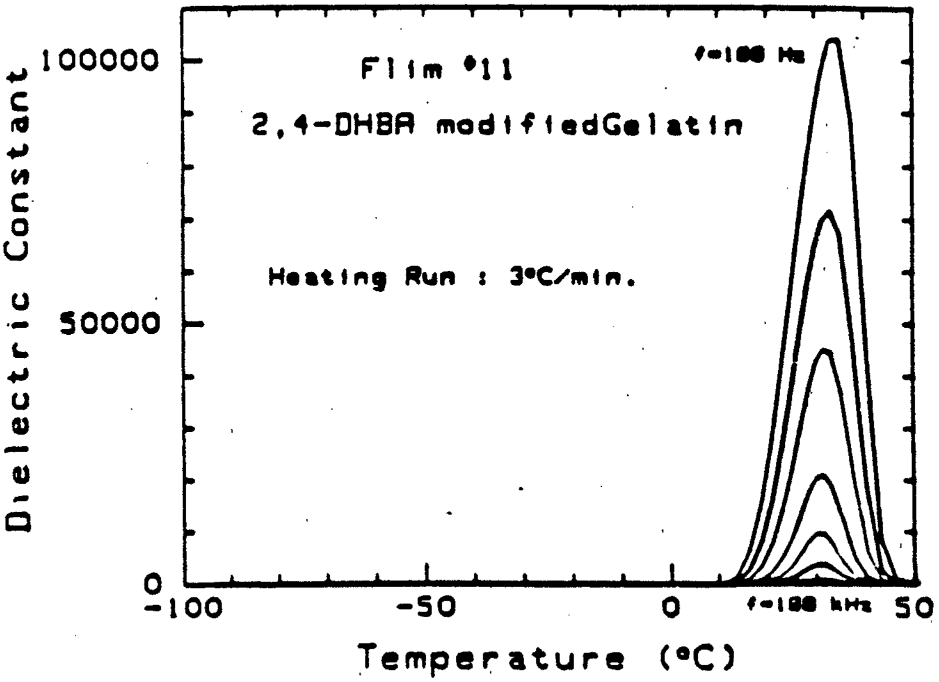
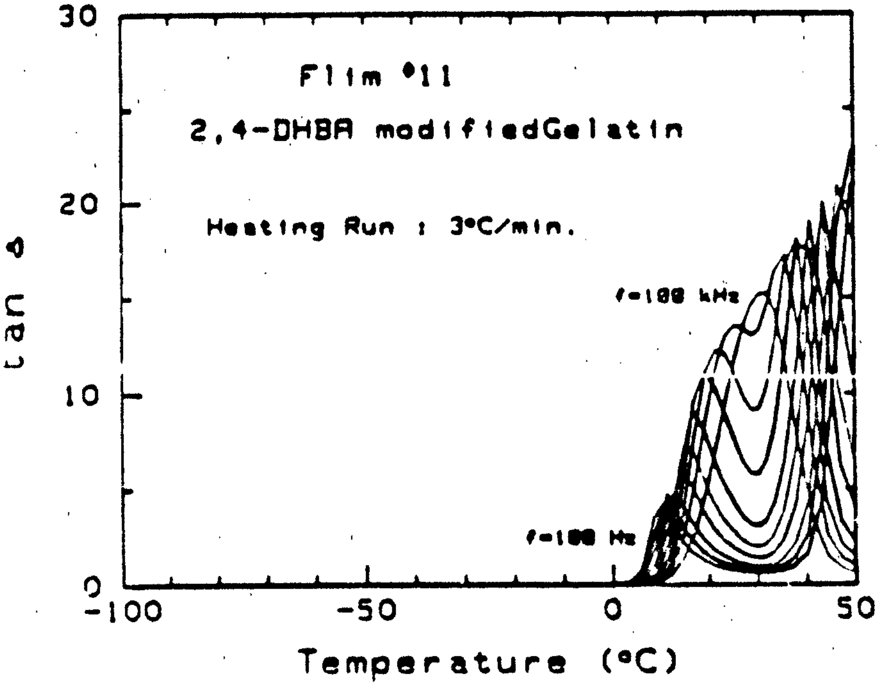


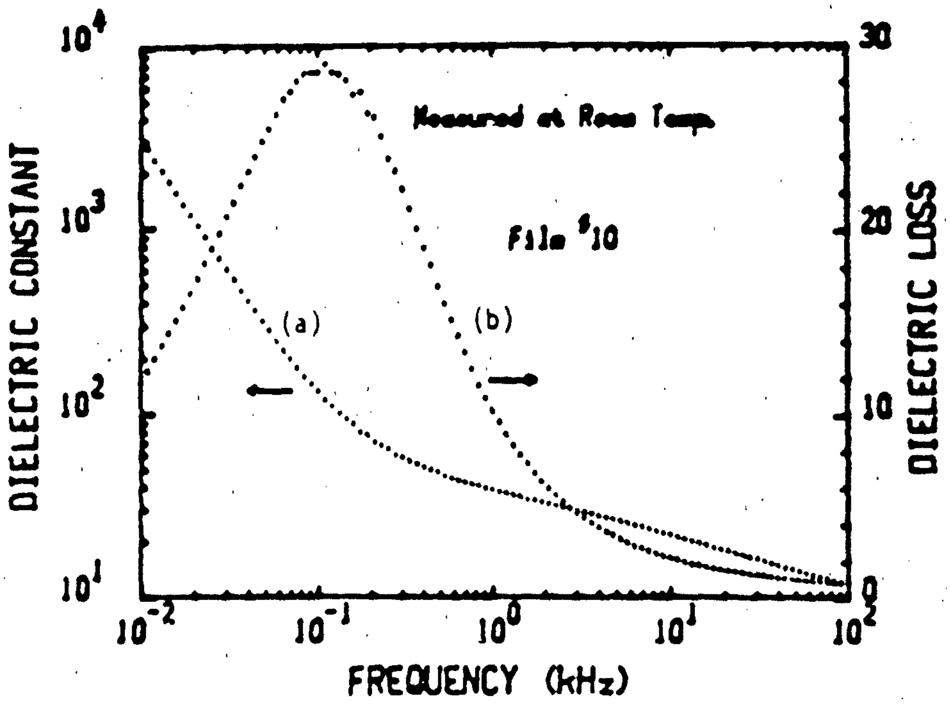
Fig 15(a)

Dielectric constant vs temperature 2,4 DHBA modified gelatin. Heating run 3°C/min. frequency 100 Hz to 100 KHz.



Dielectric loss vs temperature.

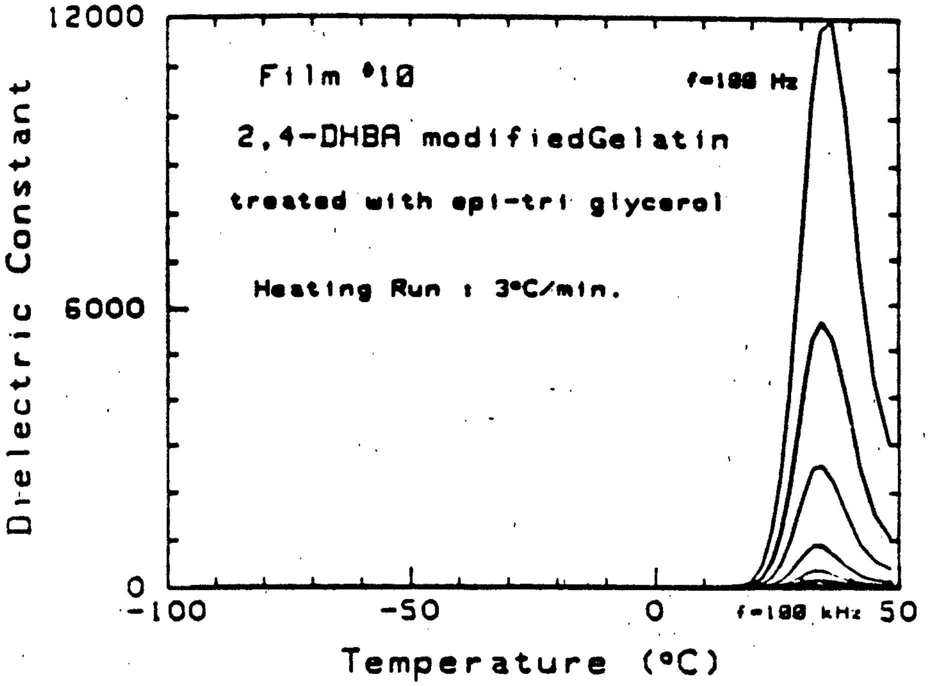
Fig 15(b)



Dielectric constant vs log frequency in 2,4 dihydroxy benzaldehyde modified gelatin treated with epi-triglycerin.

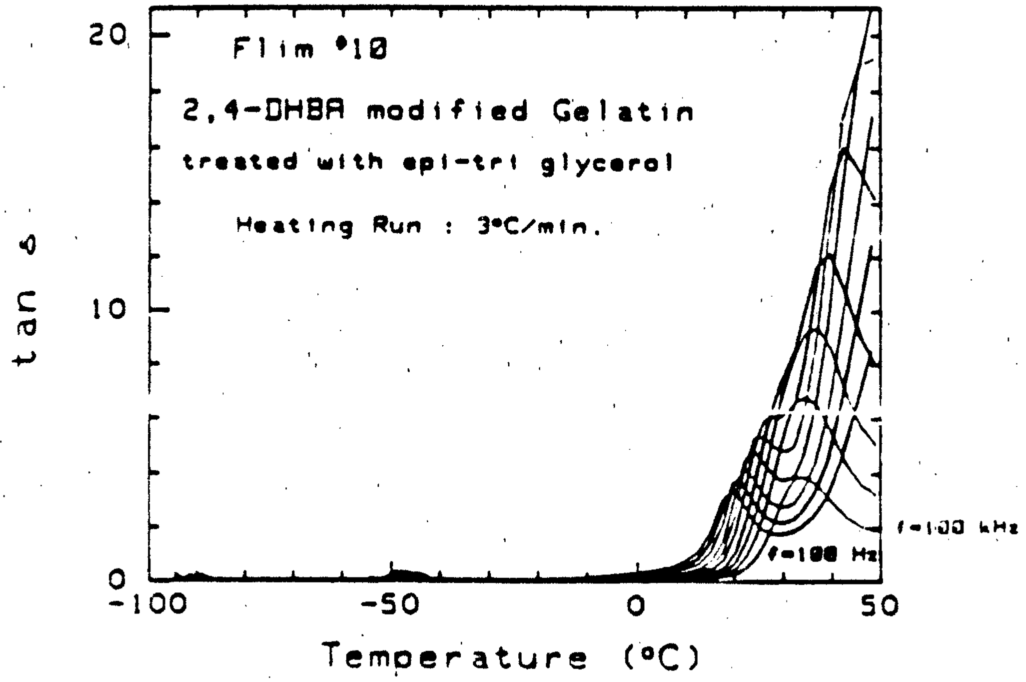
Dielectric loss vs log frequency.

Fig 16



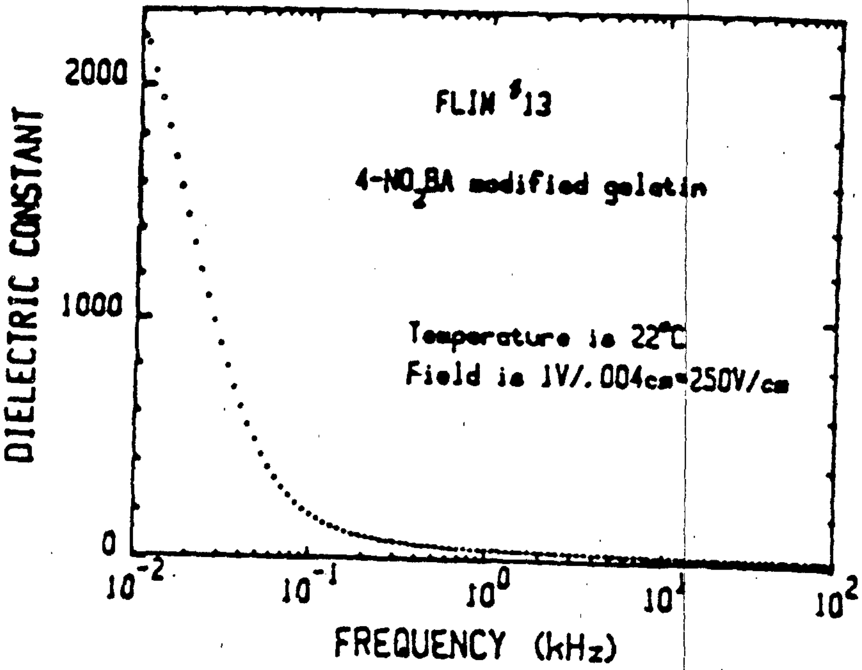
Dielectric constant vs temperature.

Fig 17(a)



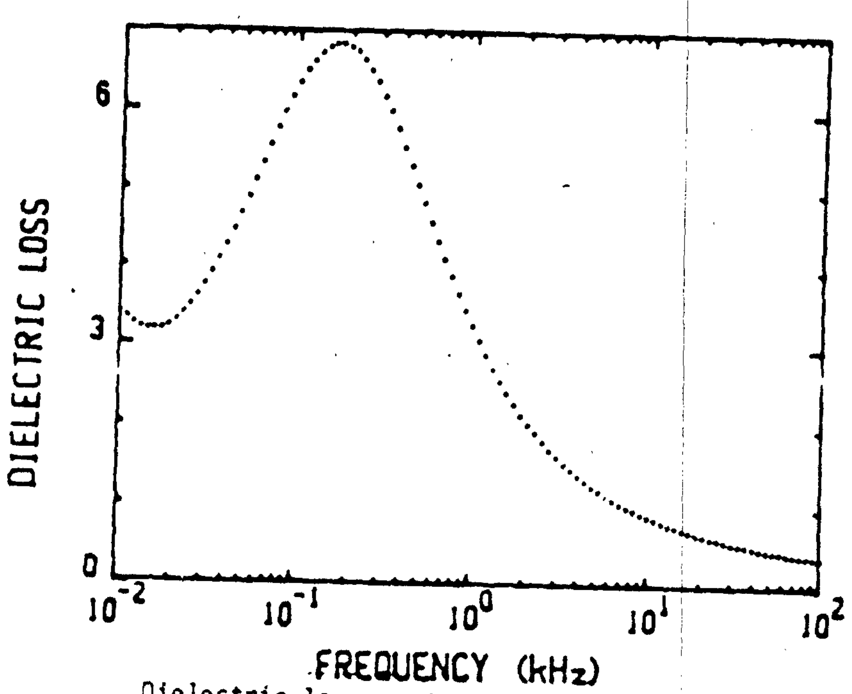
Dielectric loss vs temperature.

Fig 17(b)



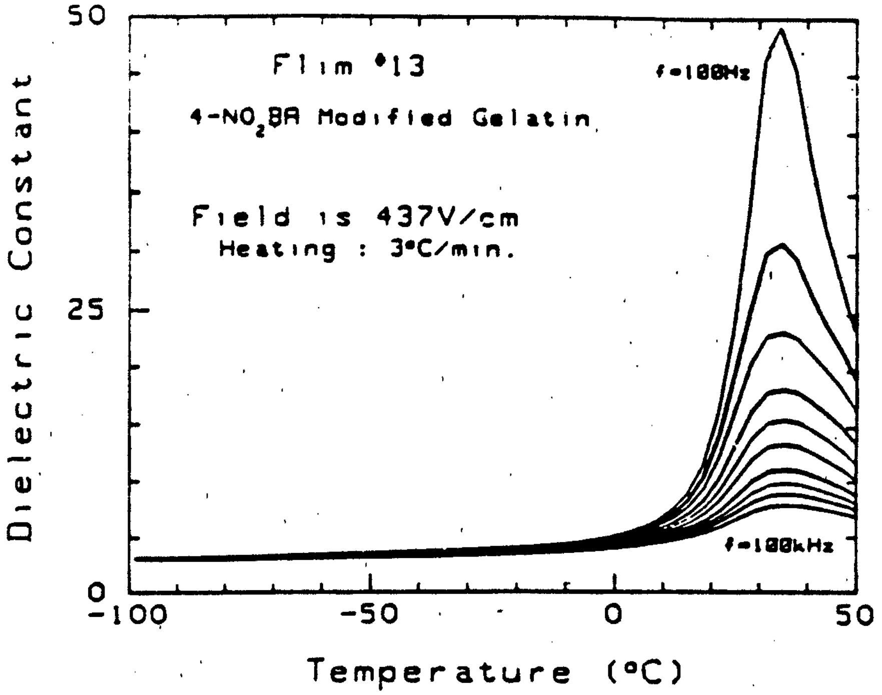
Dielectric constant vs frequency in
4-nitrobenzaldehyde modified gelatin.

Fig 18(a)



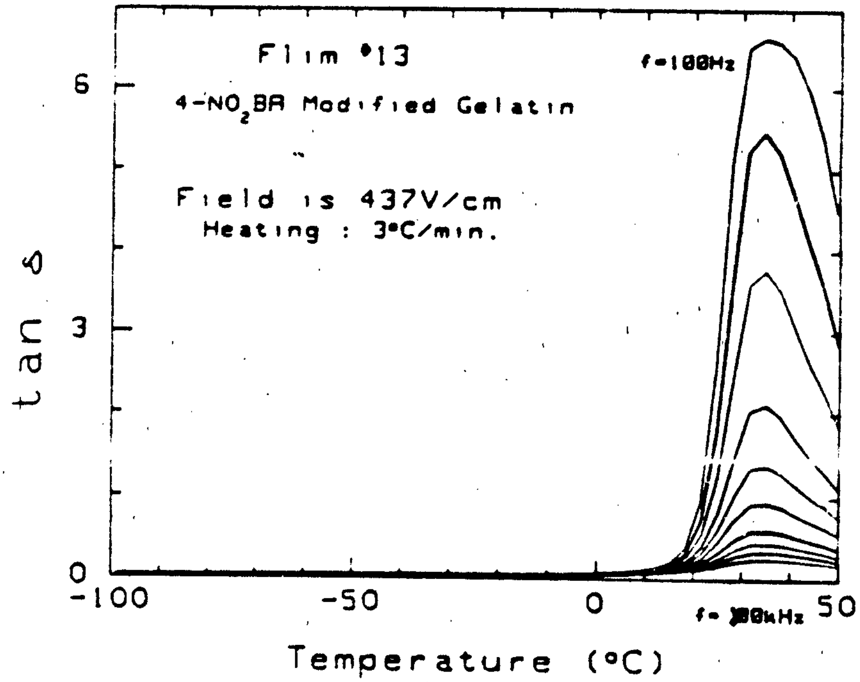
Dielectric loss vs frequency

Fig 8(b)



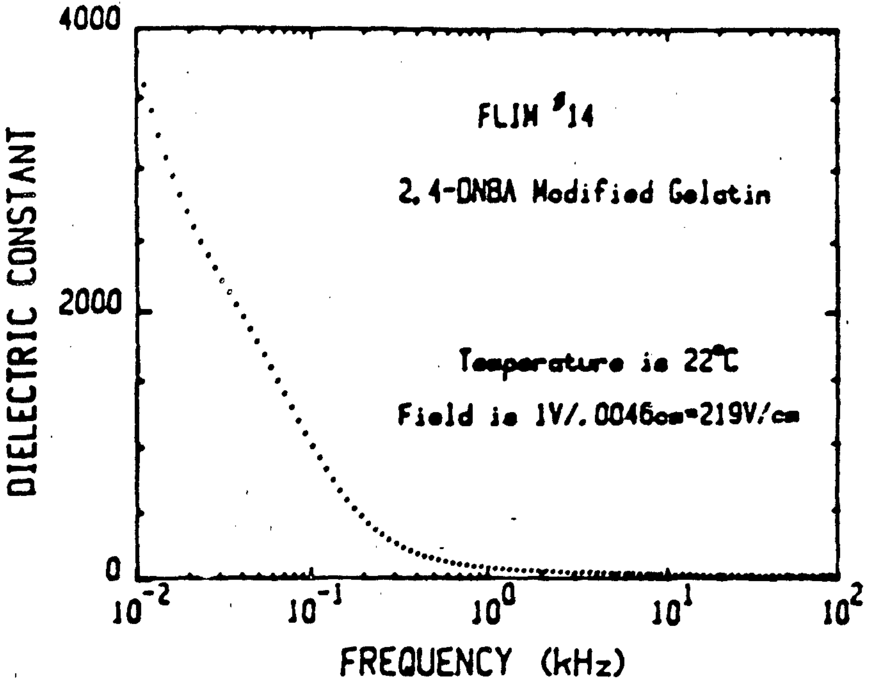
Dielectric constant vs temperature in 4- nitrobenzaldehyde modified gelatin. Room temperature 22°C AC field 437 V/cm.

Fig 19(a)



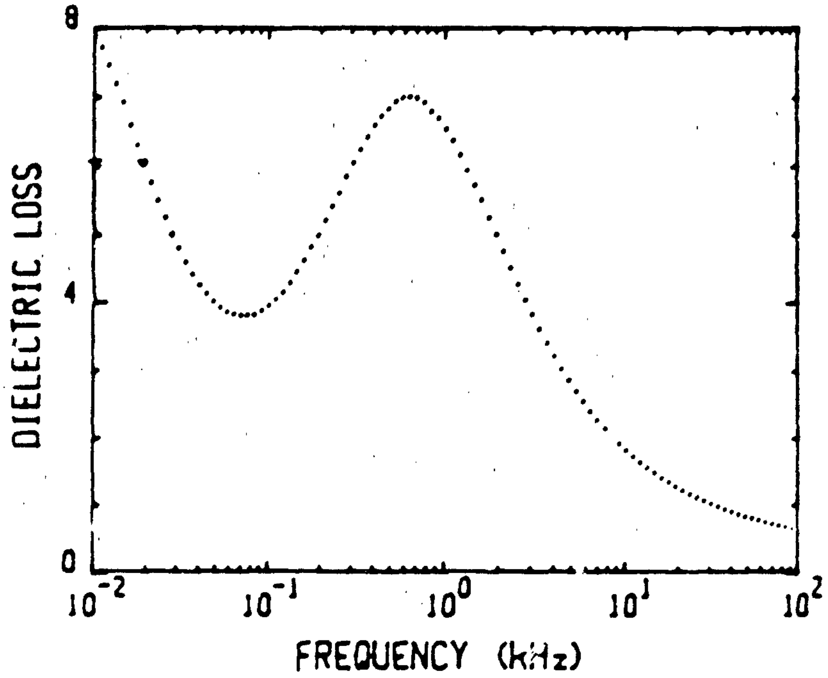
Dielectric loss vs temperature.

Fig 19(b)



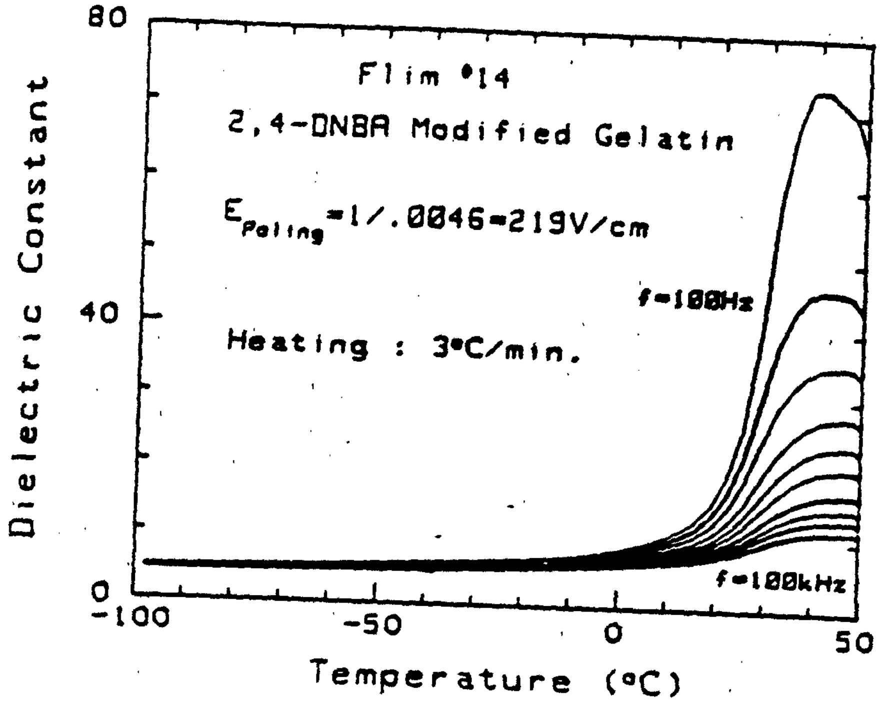
Dielectric constant vs frequency in 2,4 dinitrobenzaldehyde modified gelatin at 22°C , field 219 V/cm.

Fig 20(a)



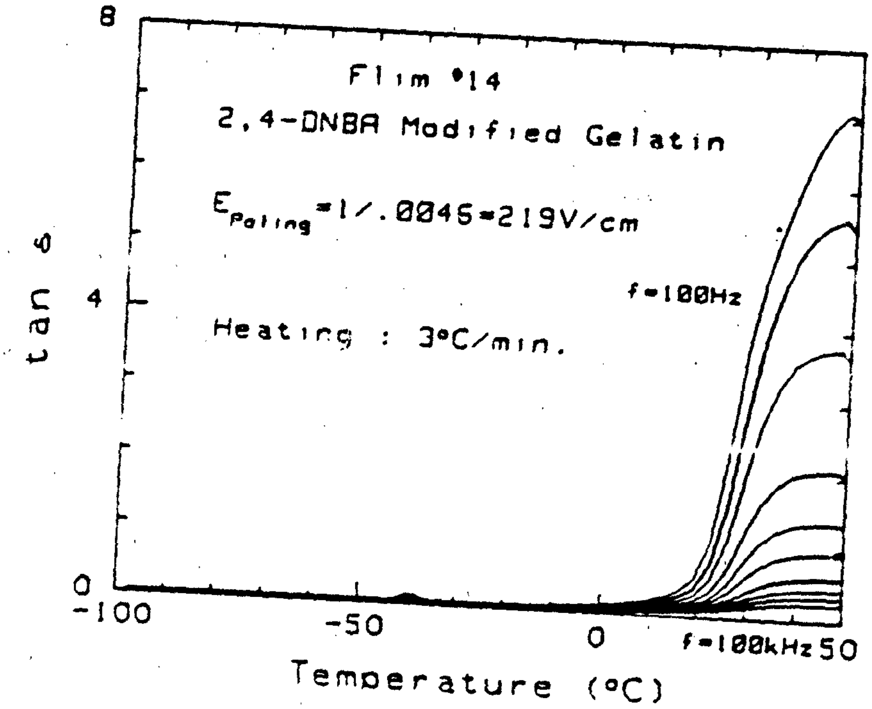
Dielectric loss vs frequency.

Fig 20(b)



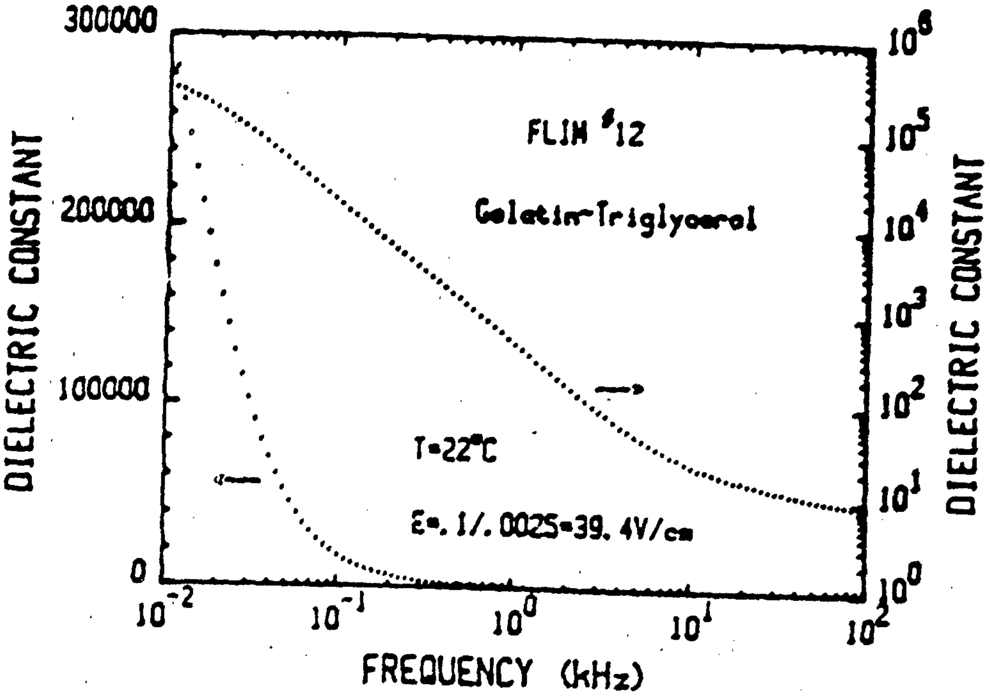
Dielectric constant vs temperature in 2,4 dinitrobenzaldehyde modified gelatin. Frequency range 100 Hz to 100 KHz.

Fig 21(a)



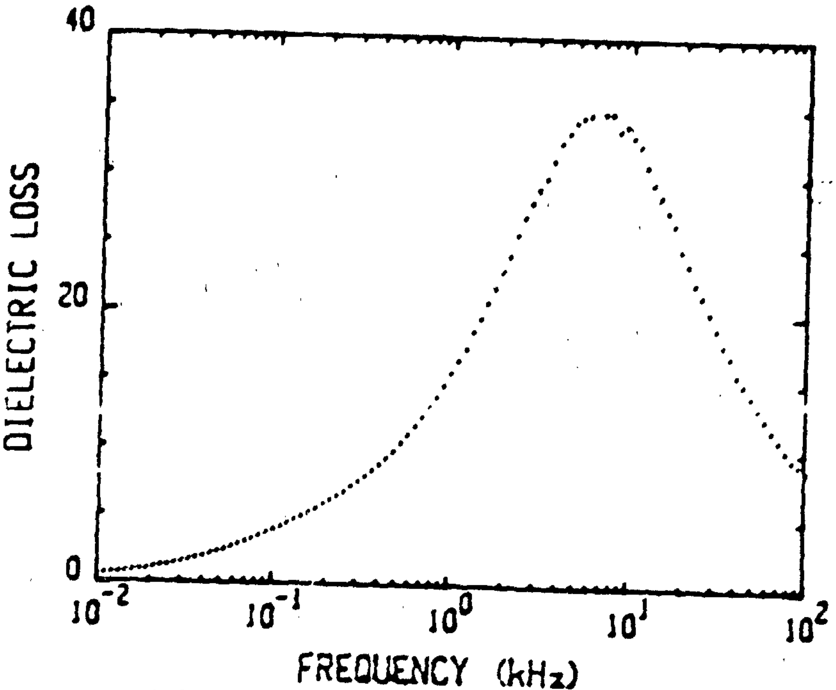
Dielectric loss vs temperature.

Fig 21(b)



Triglycerine modified gelatin. Dielectric constant vs frequency at 22°C.

Fig 22(a)



Dielectric loss vs frequency.

Fig 22(b)

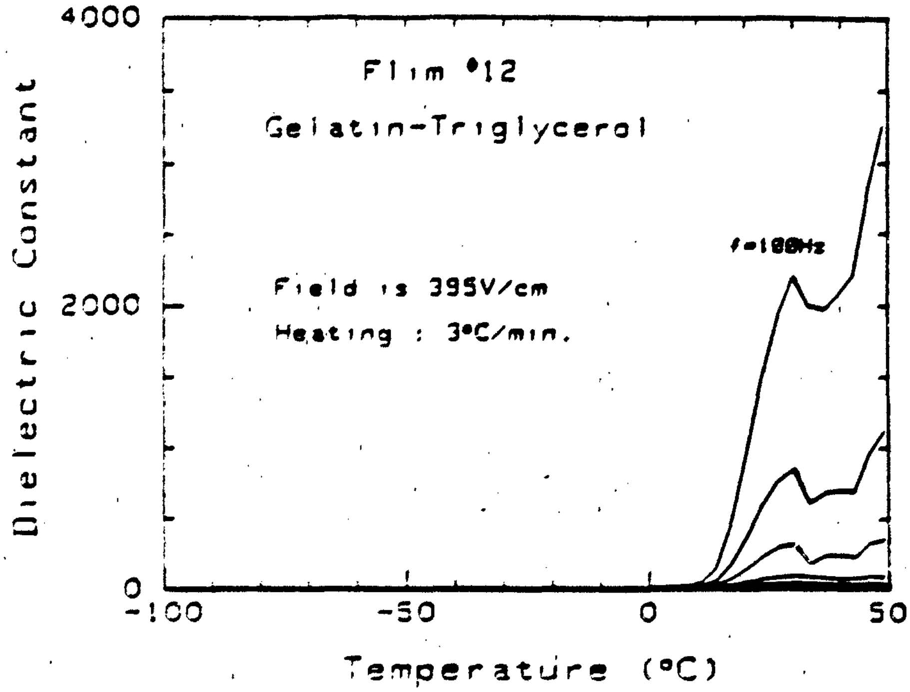


Fig 23(a)

Fig 10a Dielectric constant vs temperature
Triglycerine modified gelatin.
frequency range 100Hz to 100kHz

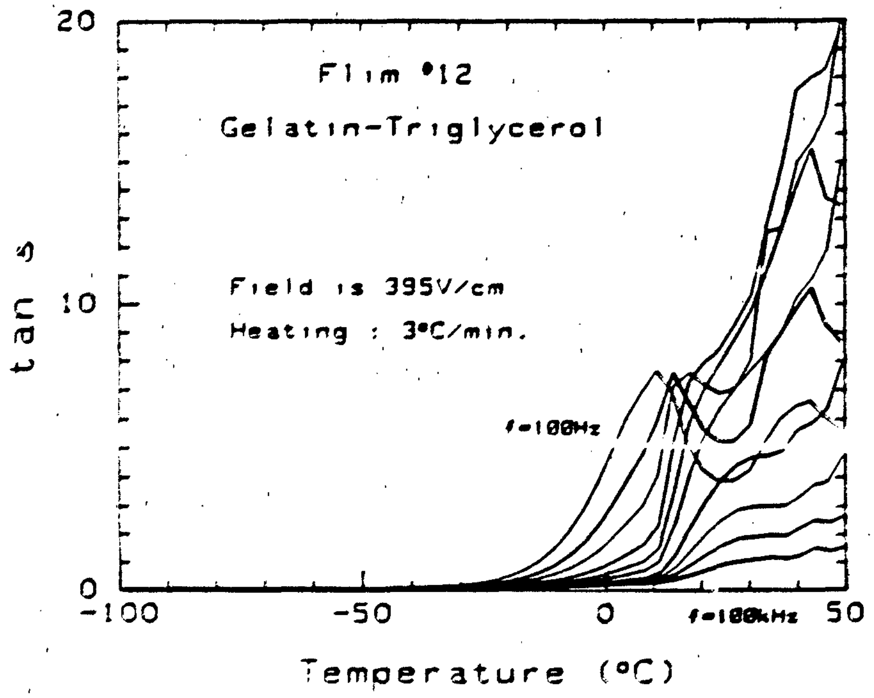


Fig 23(b)

Fig 10b Dielectric loss vs temperature

Temperature is 19°C

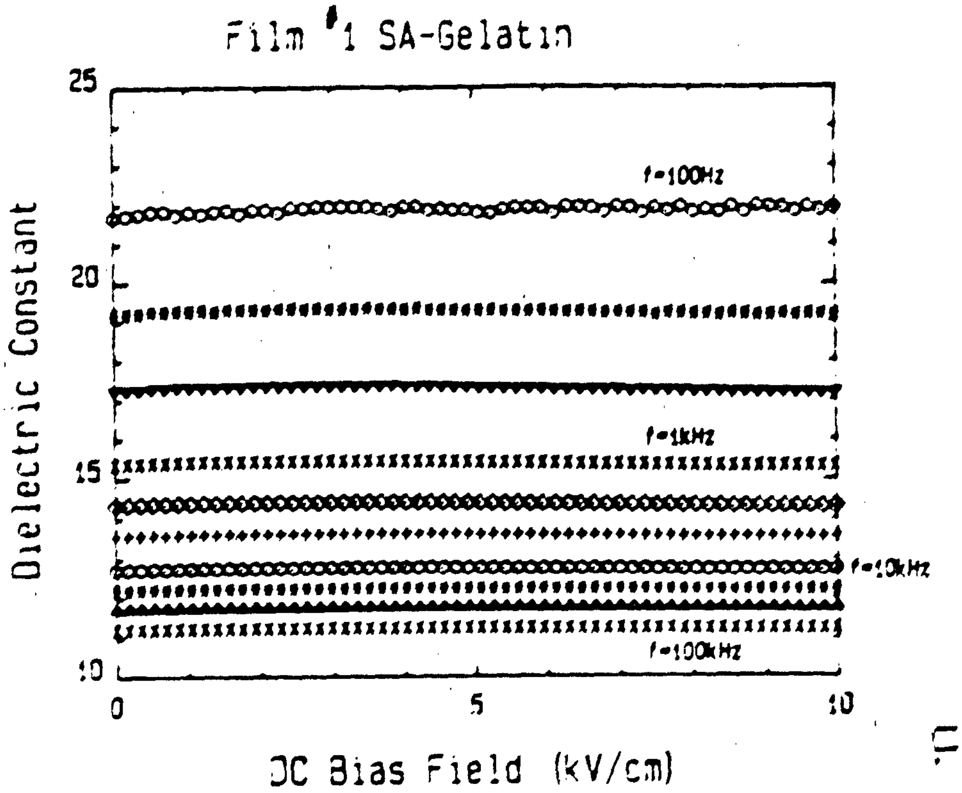


Fig 24(a)

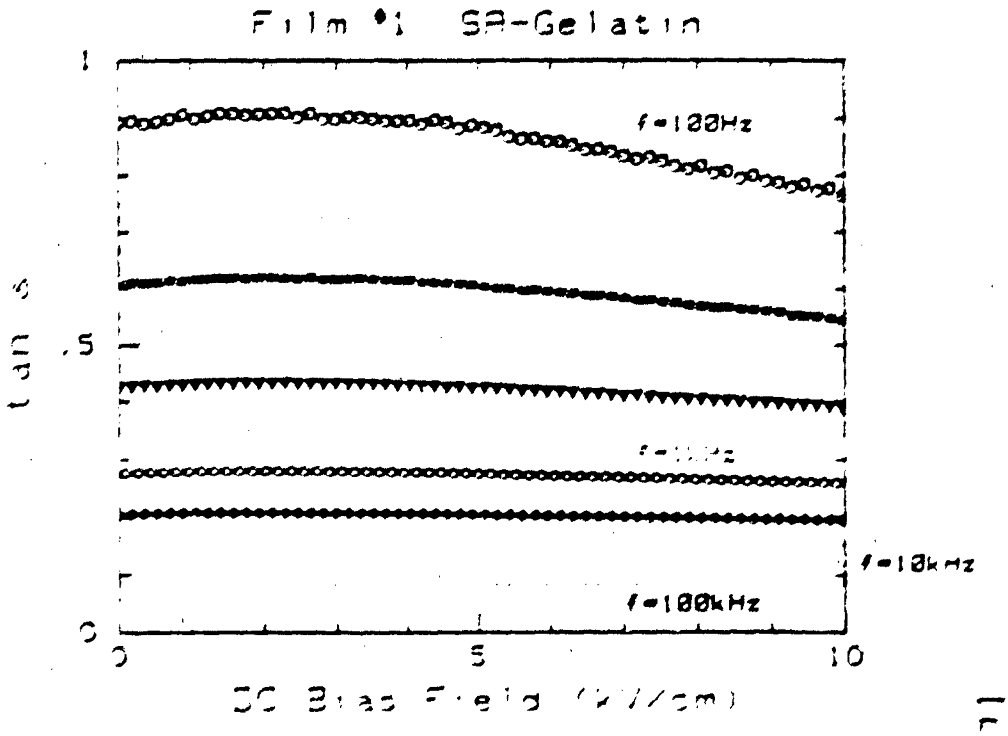


Fig 24(b)

kvS29

Temperature is 19°C

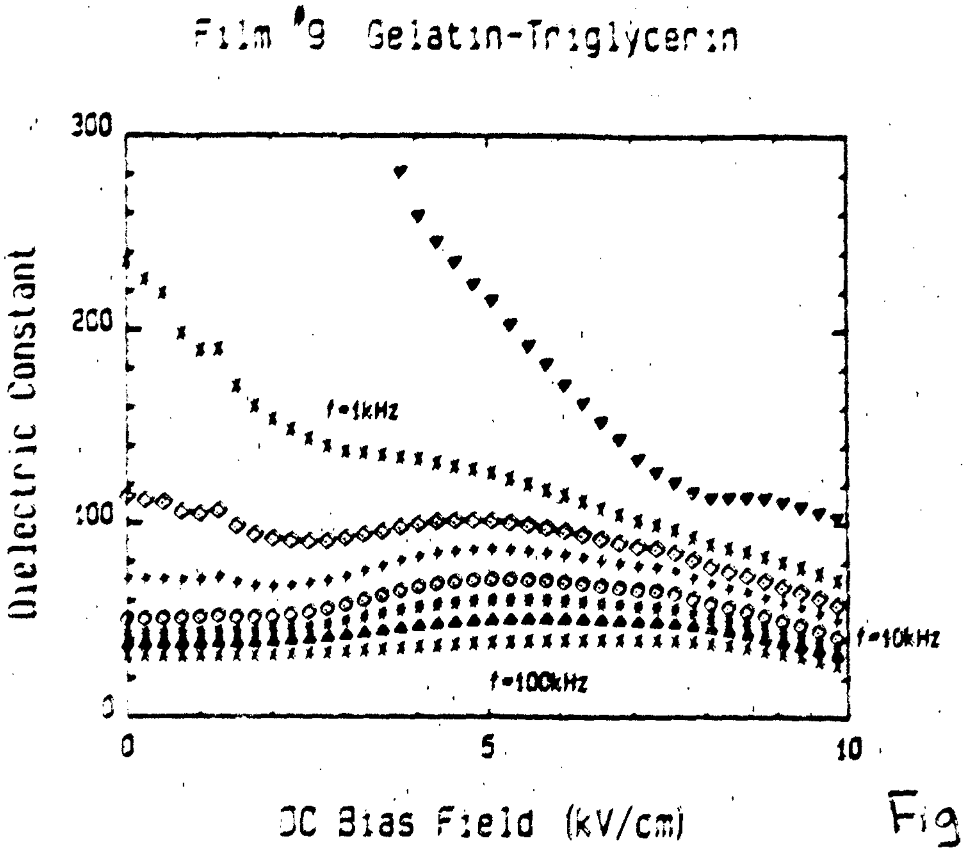


Fig 25(a)

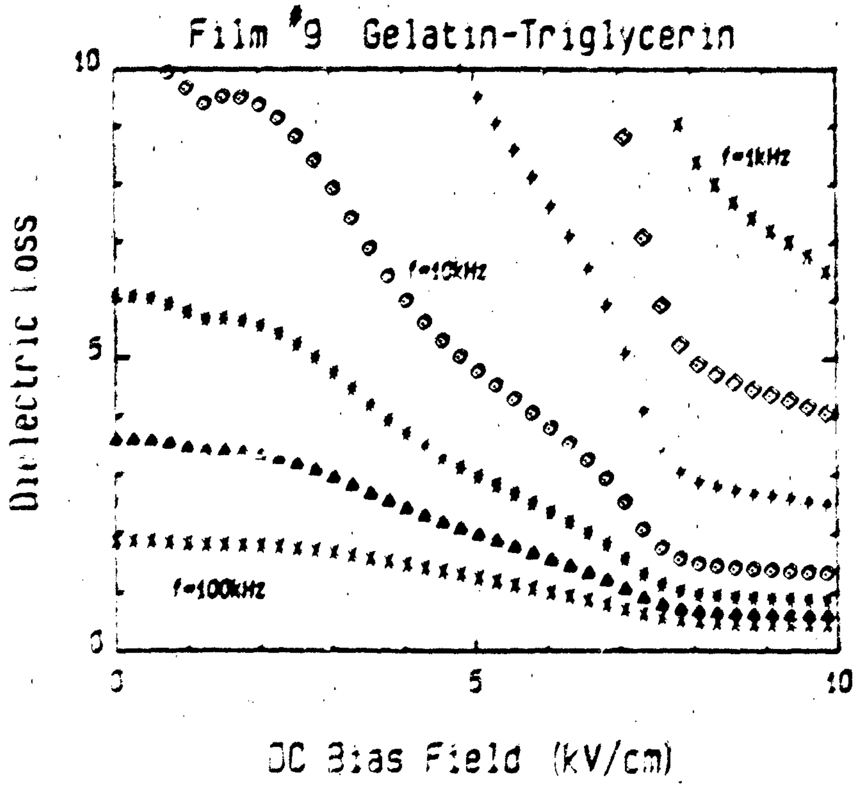


Fig 25(b)

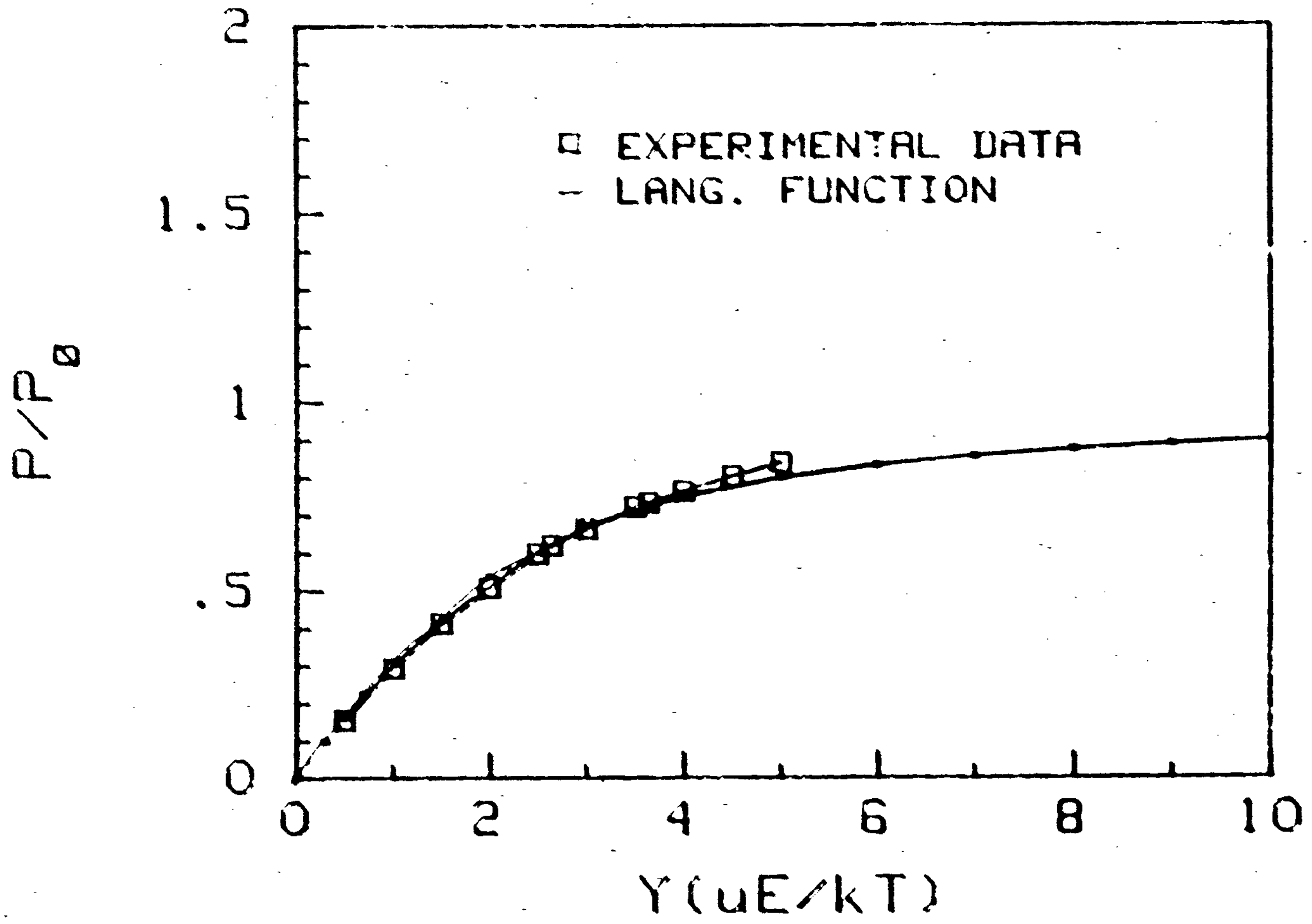


Fig 26

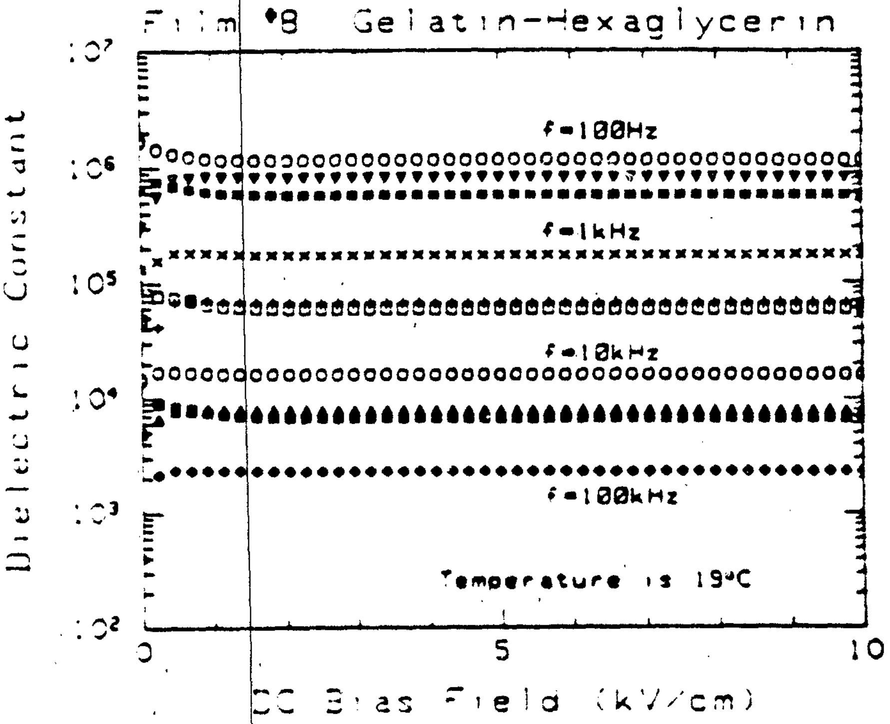


Fig 27(a)

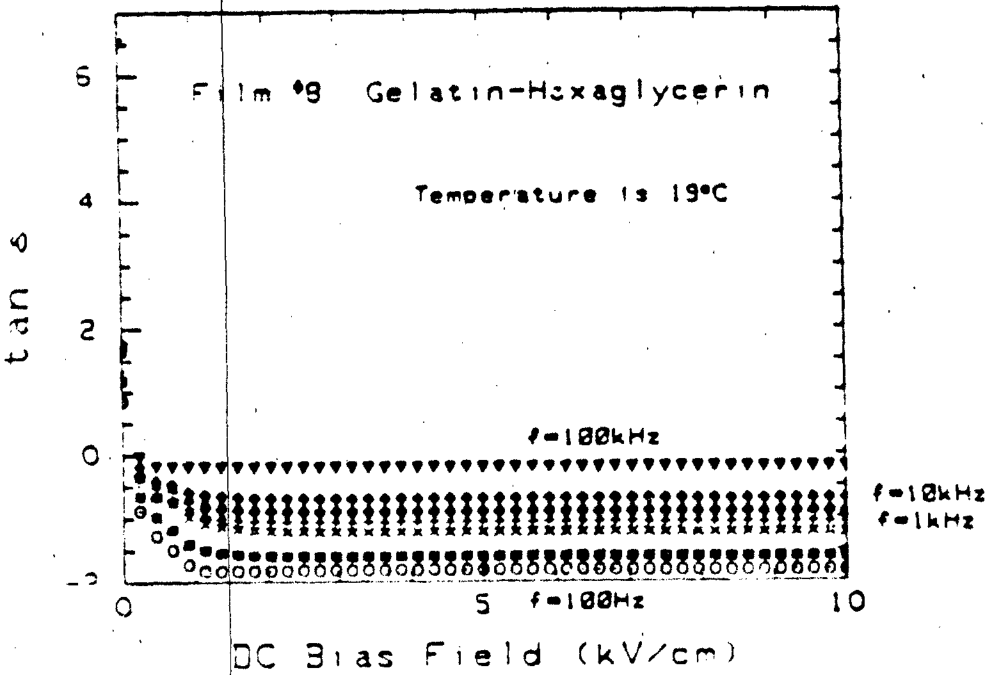


Fig 27(b)

KVSE:4

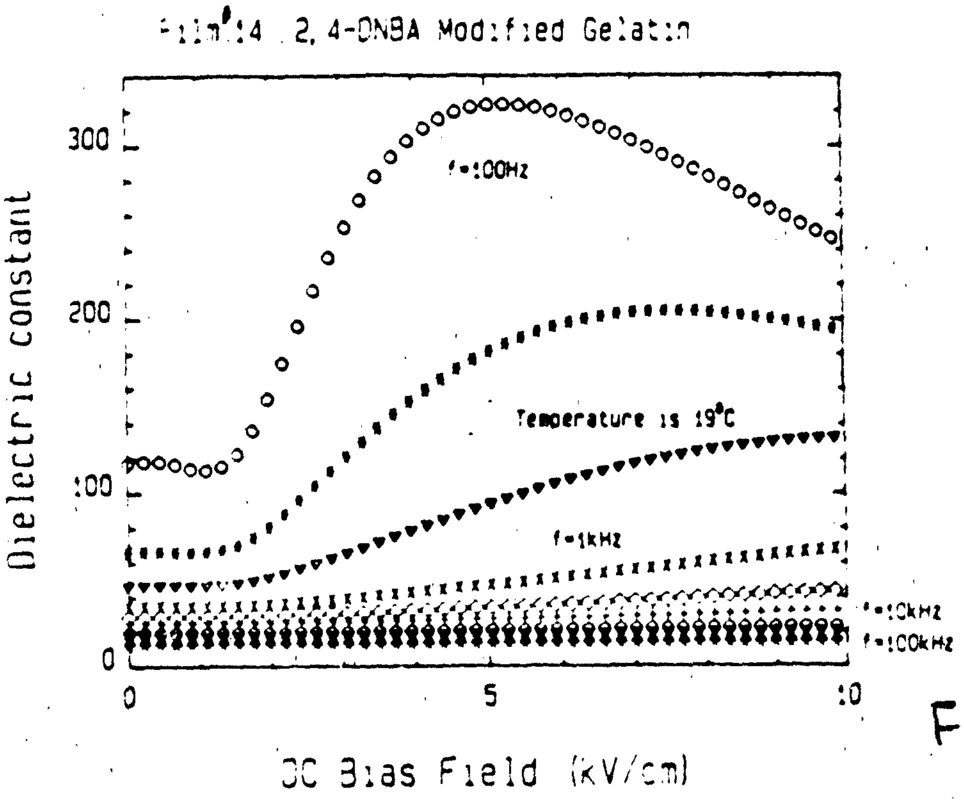


Fig 28(a)

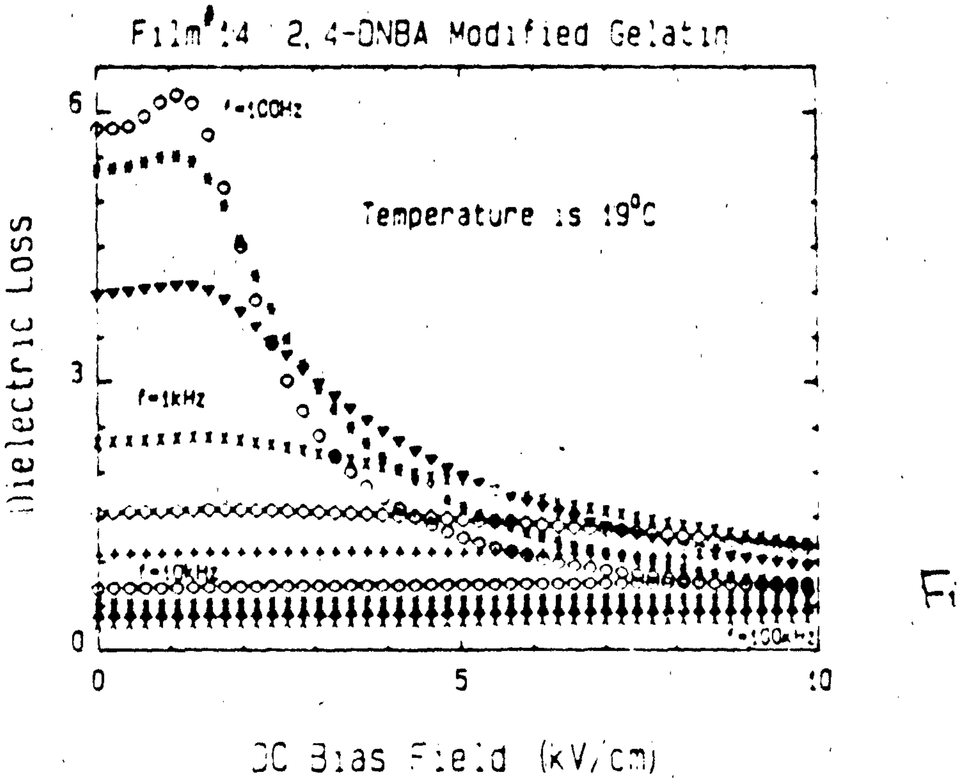
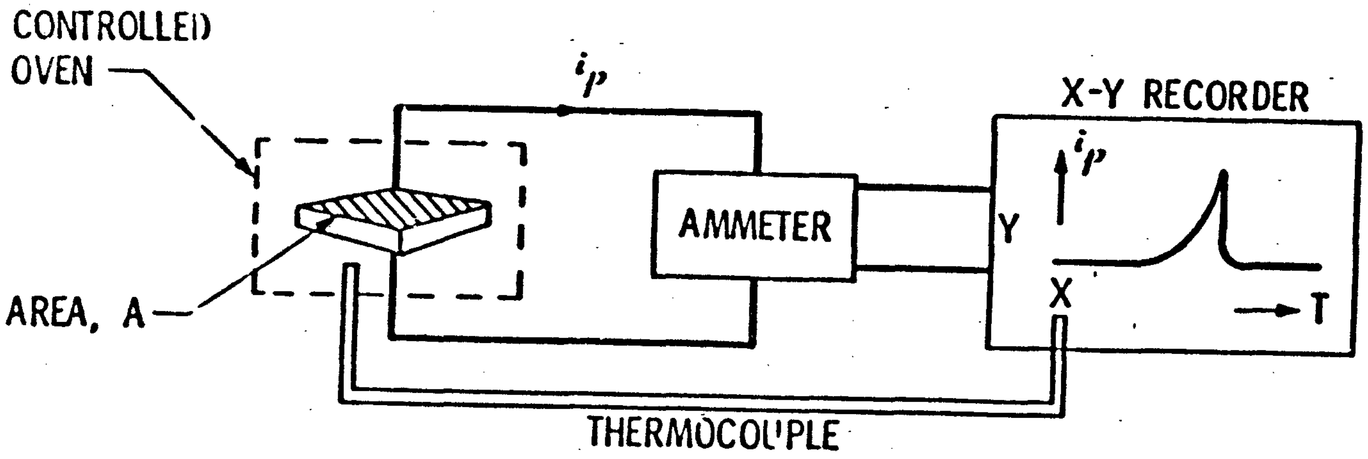


Fig 28(b)

# PYROELECTRIC MEASUREMENT

<u>BYER-ROUNDY TECHNIQUE</u> - MEASURES THE MAGNITUDE AND TEMPERATURE DEPENDENCE OF THE PYROELECTRIC COEFFICIENT, $p \equiv dP_s/dT$



$$p(T) = \frac{i_p}{A\,dT/dt}$$

- SAMPLE HEATED LINEARLY WITH TIME, t
- PYROELECTRIC CURRENT, $i_p$, MEASURED

Fig 29

# PYROELECTRIC MATERIALS FOR IR DETECTORS

## THERMAL/OPTICAL MEASUREMENTS

CHYNOWETH TECHNIQUE - MEASURES THE DYNAMIC PYROELECTRIC RESPONSE, i.e., THE FIGURES OF MERIT $p/c_p$ AND $p/c_p\epsilon$

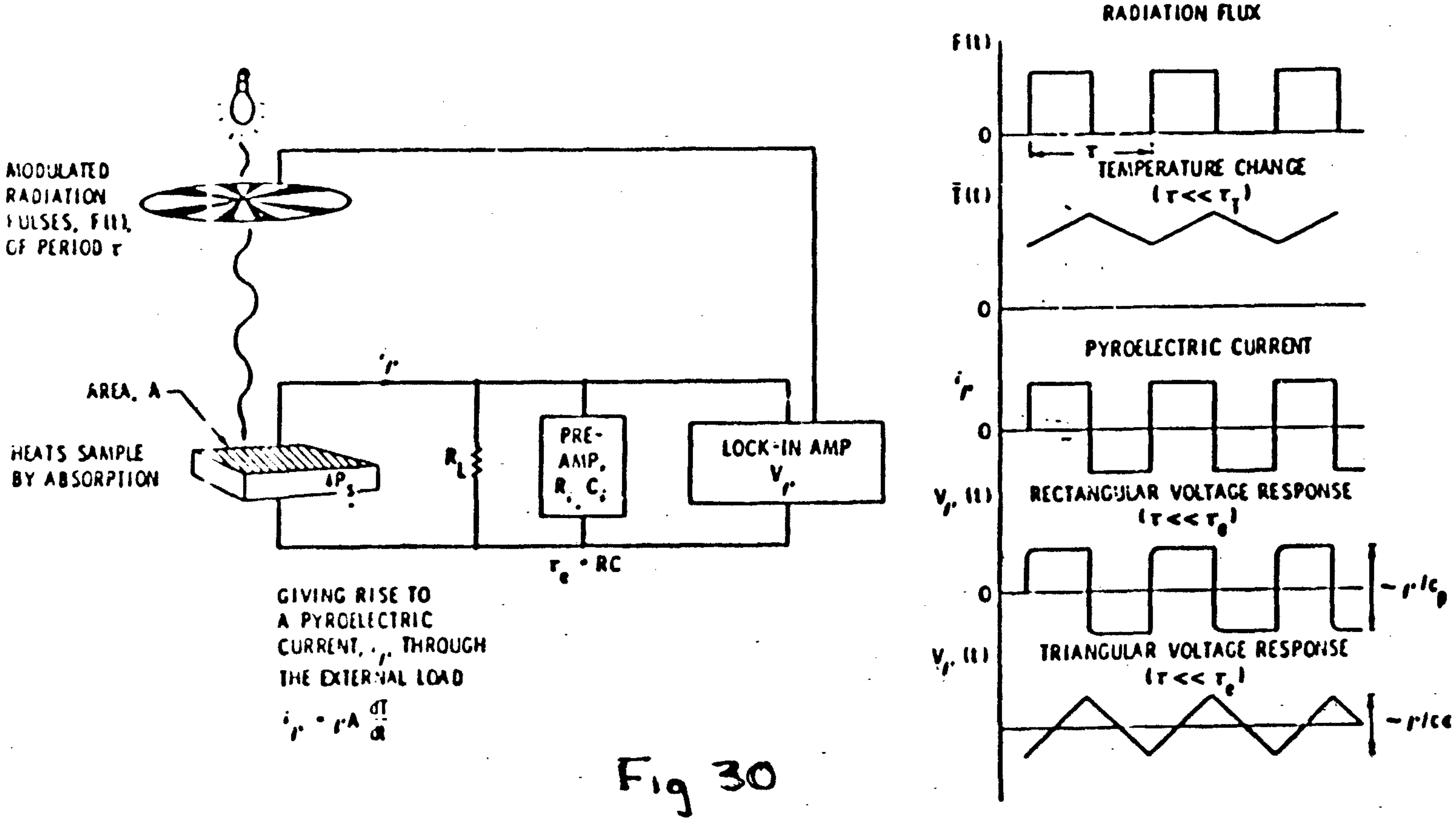


Fig 30

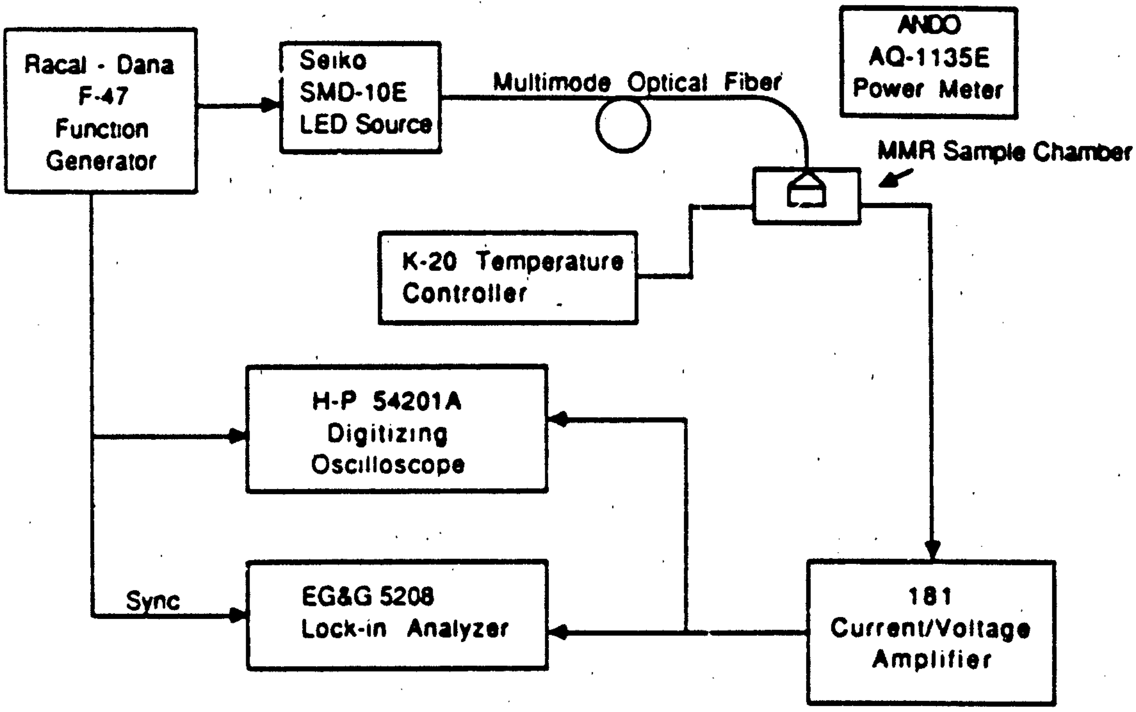
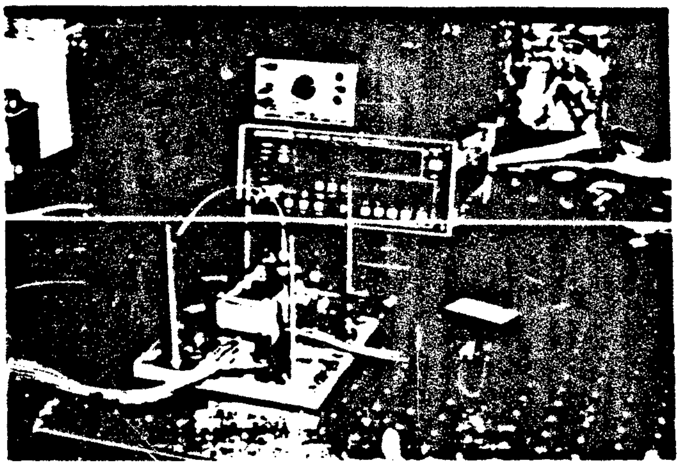


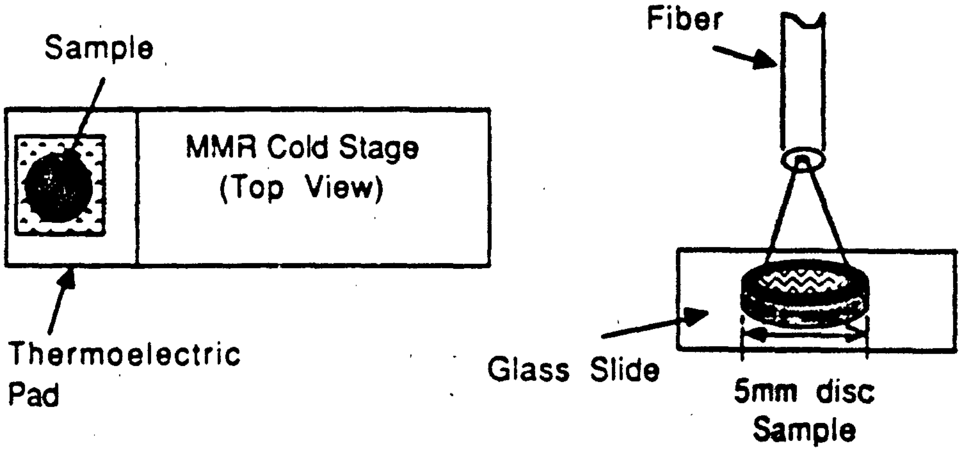
Fig 31(a)

Overall block diagram of MRL-Chynoweth System.



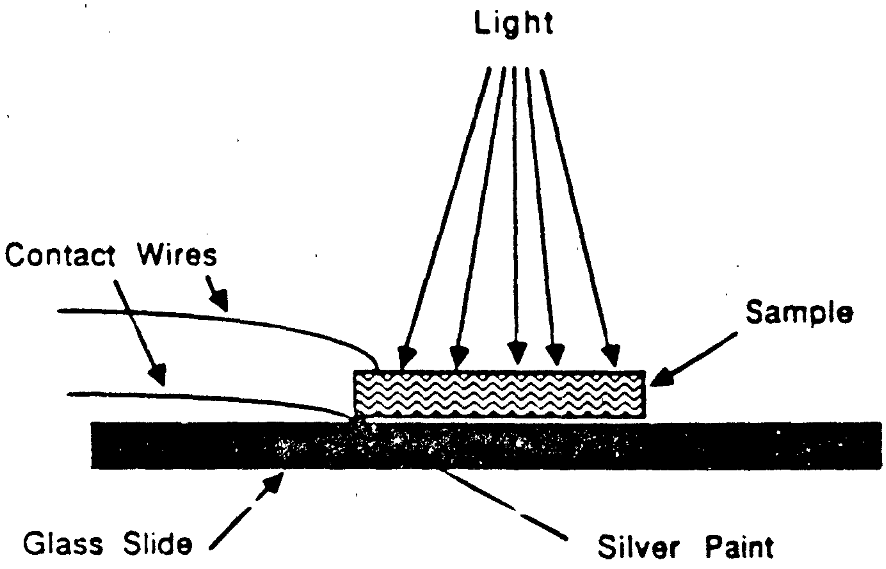
Picture of the new Chynoweth setup.

Fig 31(b)



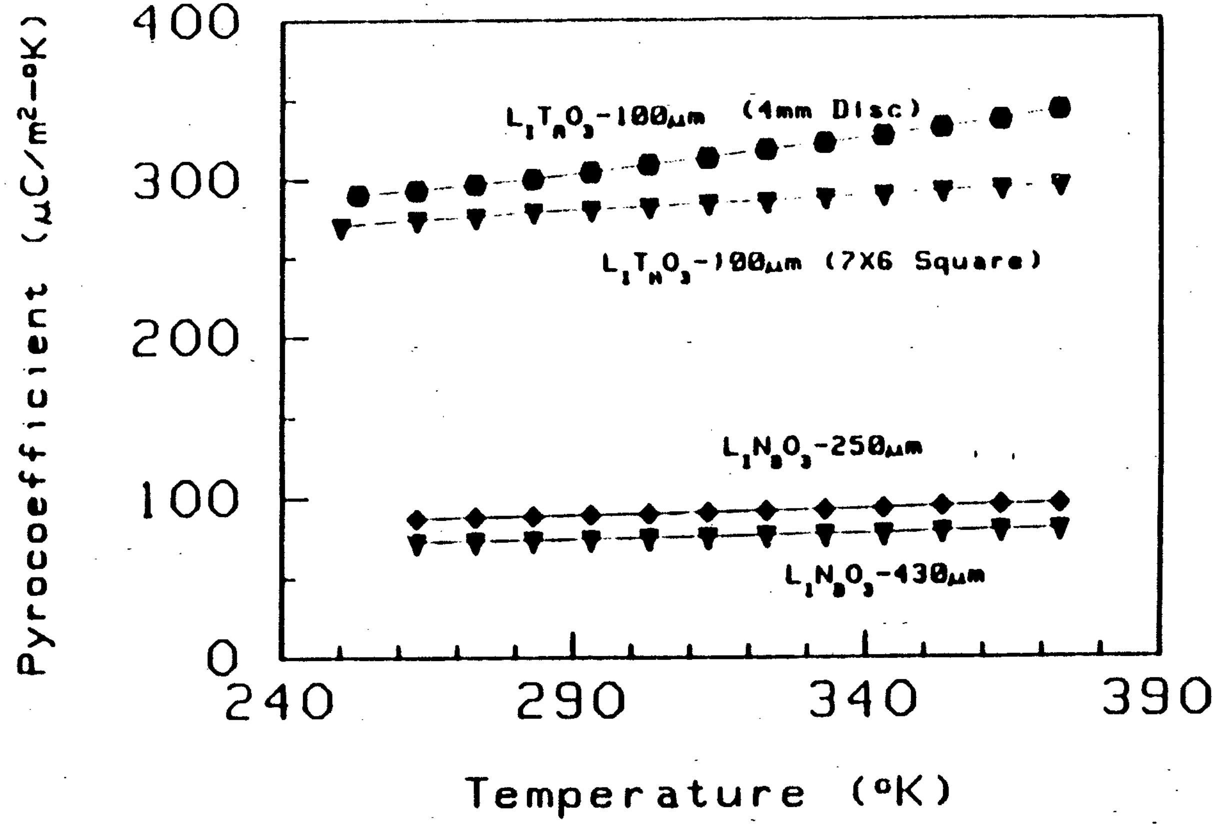
MMR thermoelectric stage and depiction of sample illumination with optical an fiber.

Fig 32(a)



Sample mounting.

Fig 32(b)



Lithium niobate pyroelectric coefficient vs temperature for two samples of different thicknesses (MRL-Chynoweth method).

Fig 33

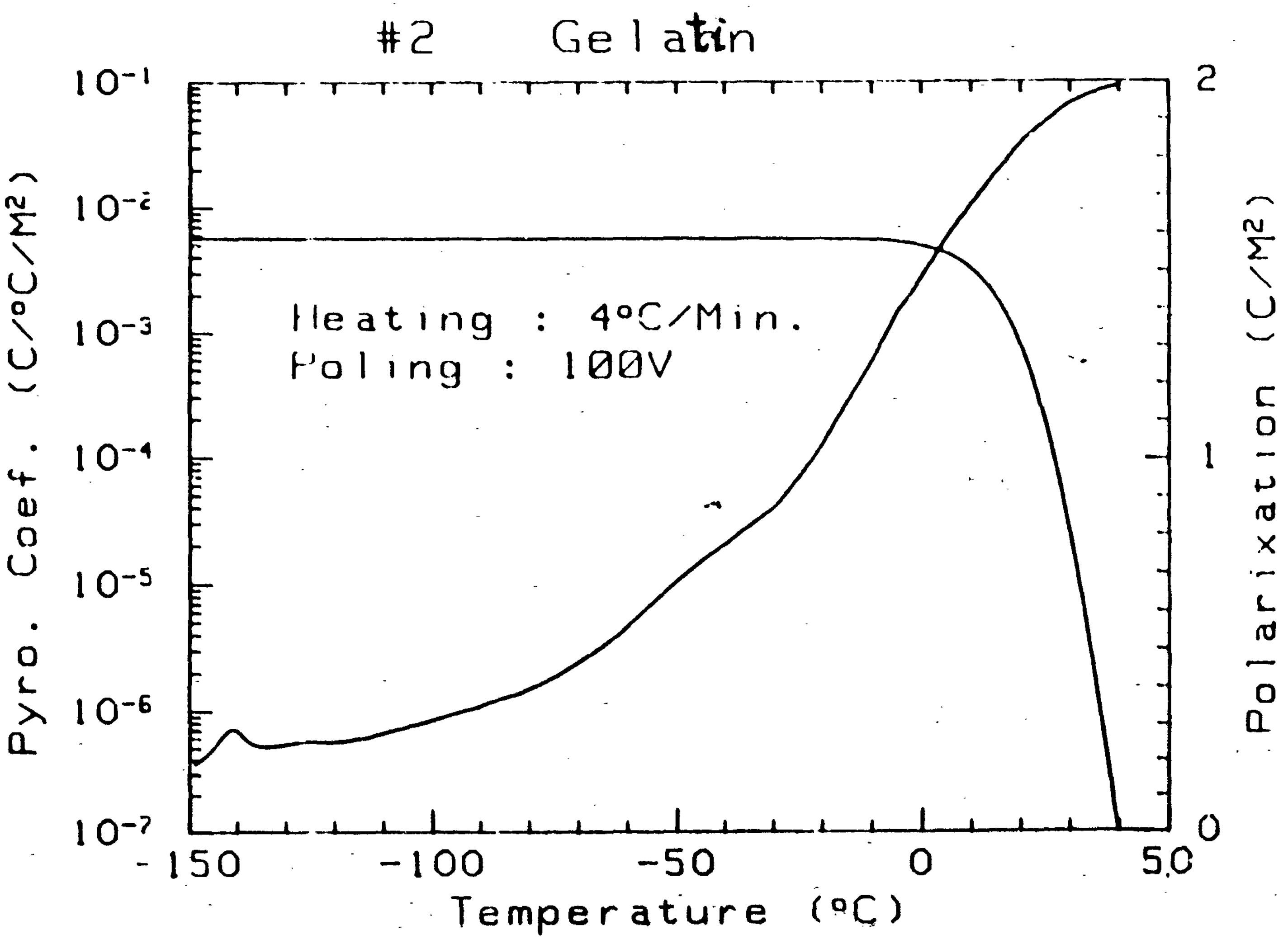
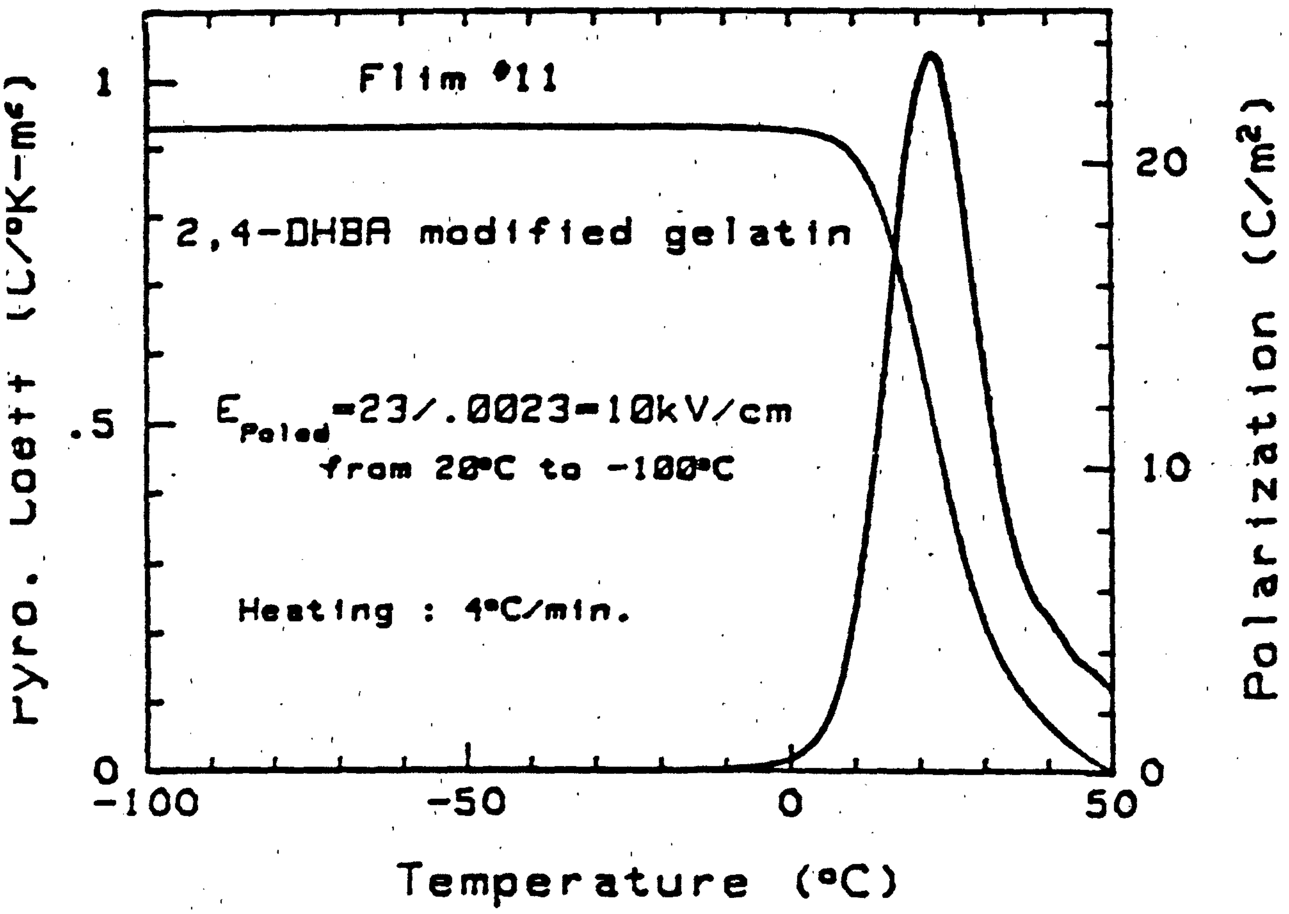
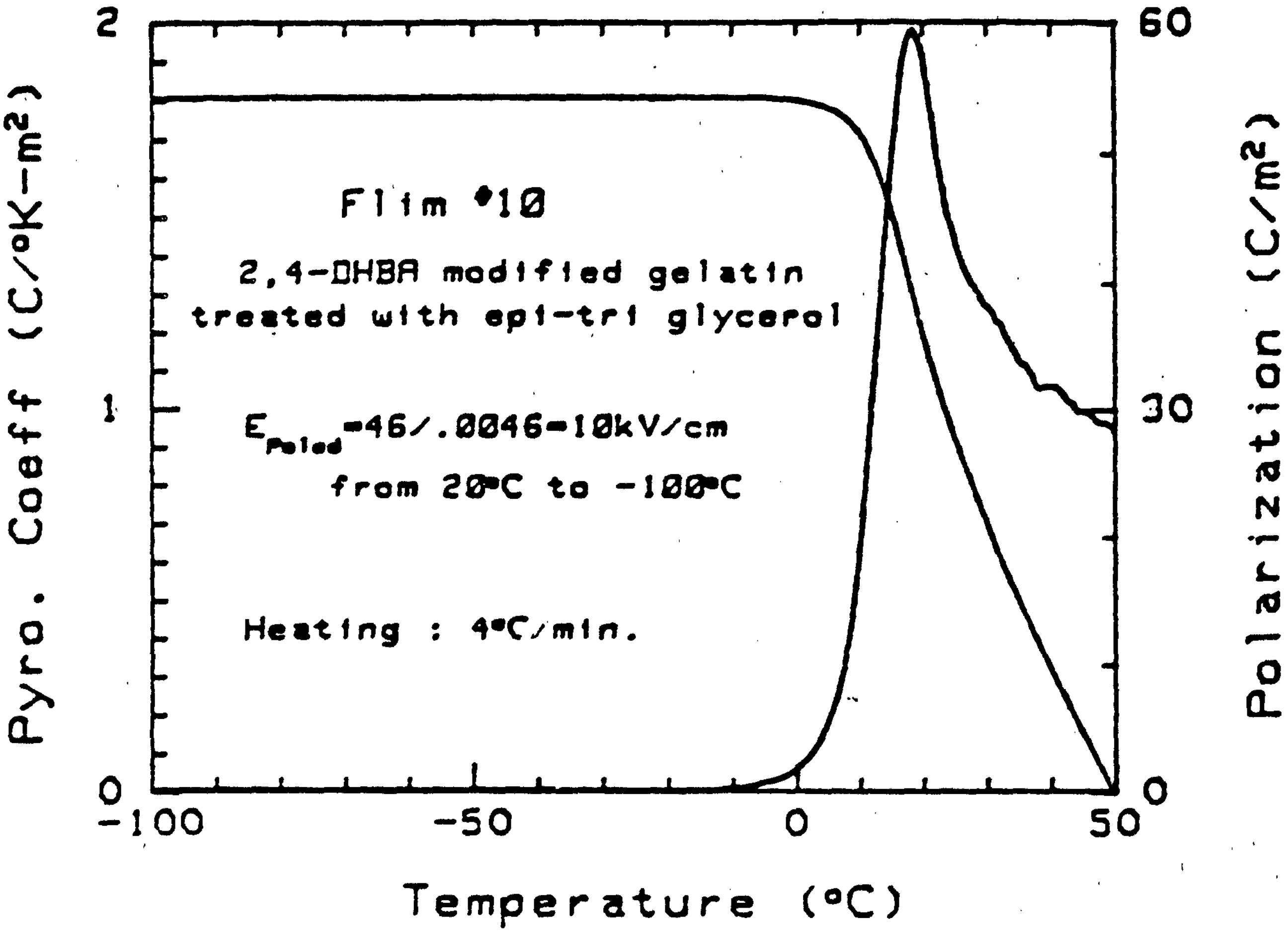

#2 Gelatin
Pyro. Coef. (C/°C/M²)
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10⁻⁷
Polarixation (C/M²)
2
1
0
Heating : 4°C/Min.
Poling : 100V
-150
-100
-50
0
50
Temperature (°C)

Fig 34



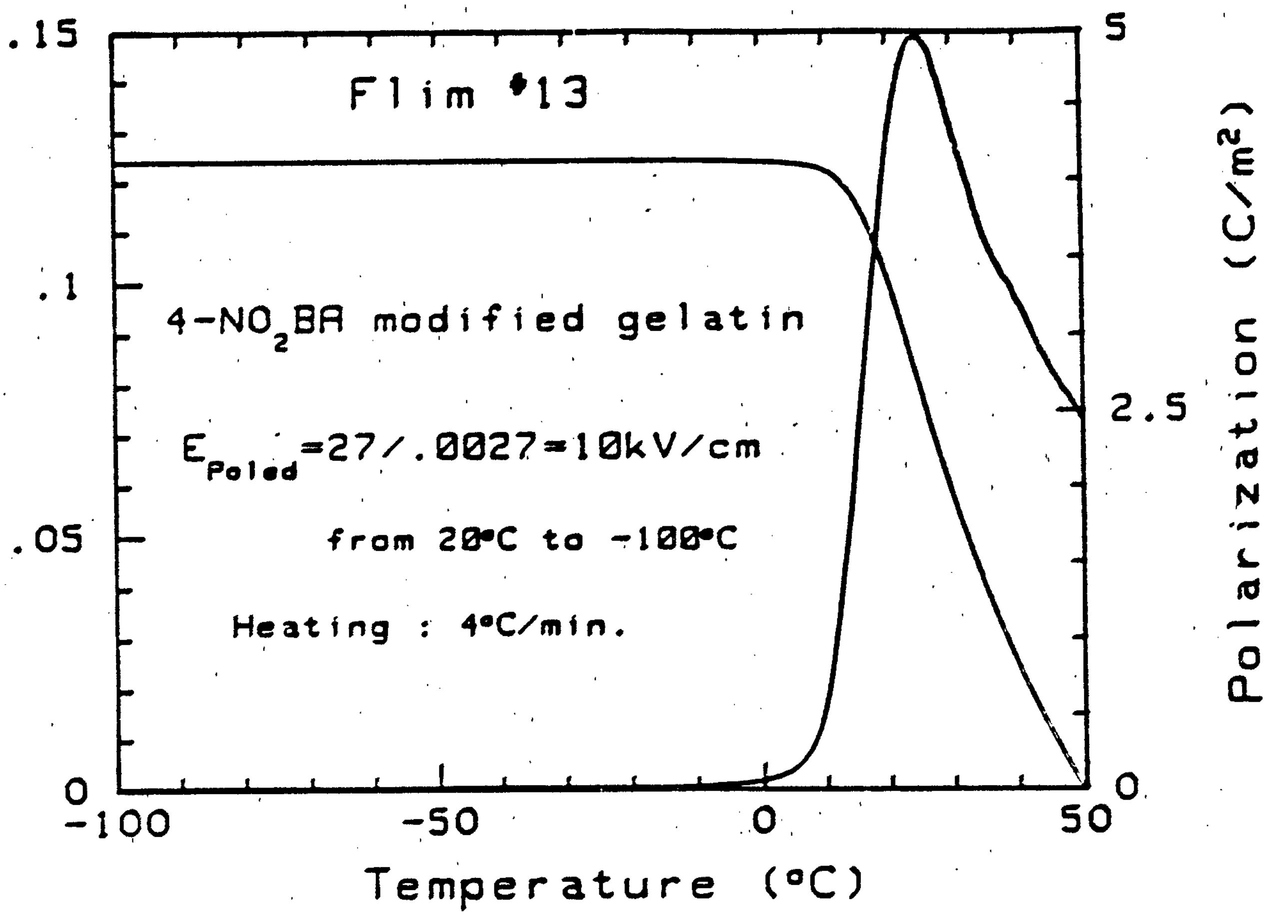
Byer-Roundy measurement of the pyroelectric coefficient and the integrated polarization in 2,4 dihydroxybenzaldehyde modified gelatin. Heating rate 4°C/min, poling field 10 kV/cm.

Fig 35



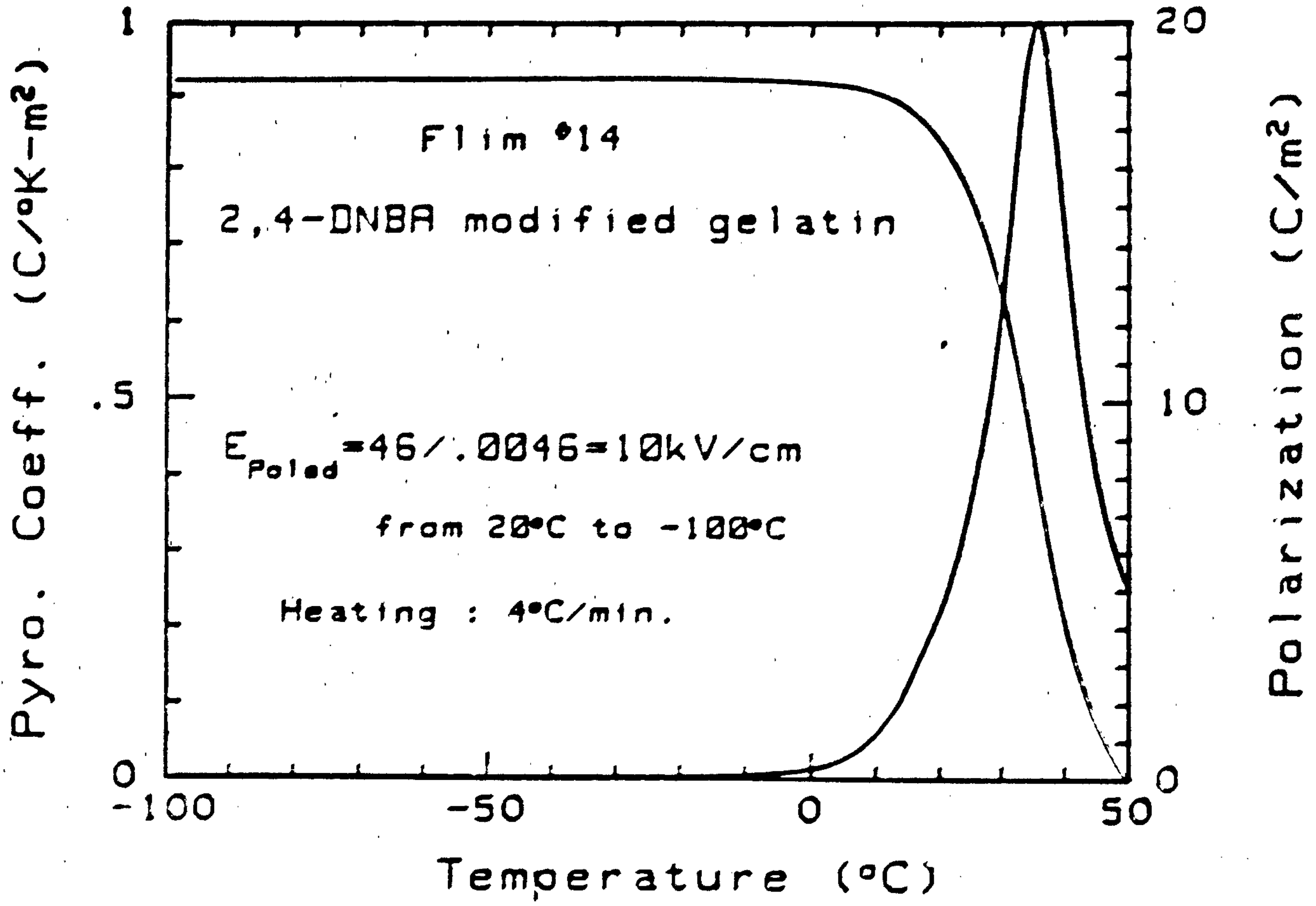
. 2,4 dihydroxybenzaldehyde modified gelatin treated with epi-triglycerin. Byer-Roundy measurement of the pyroelectric coefficient and integrated polarization. Heating rate 4°C/min., Poling field 10 kV/cm.

Fig 36



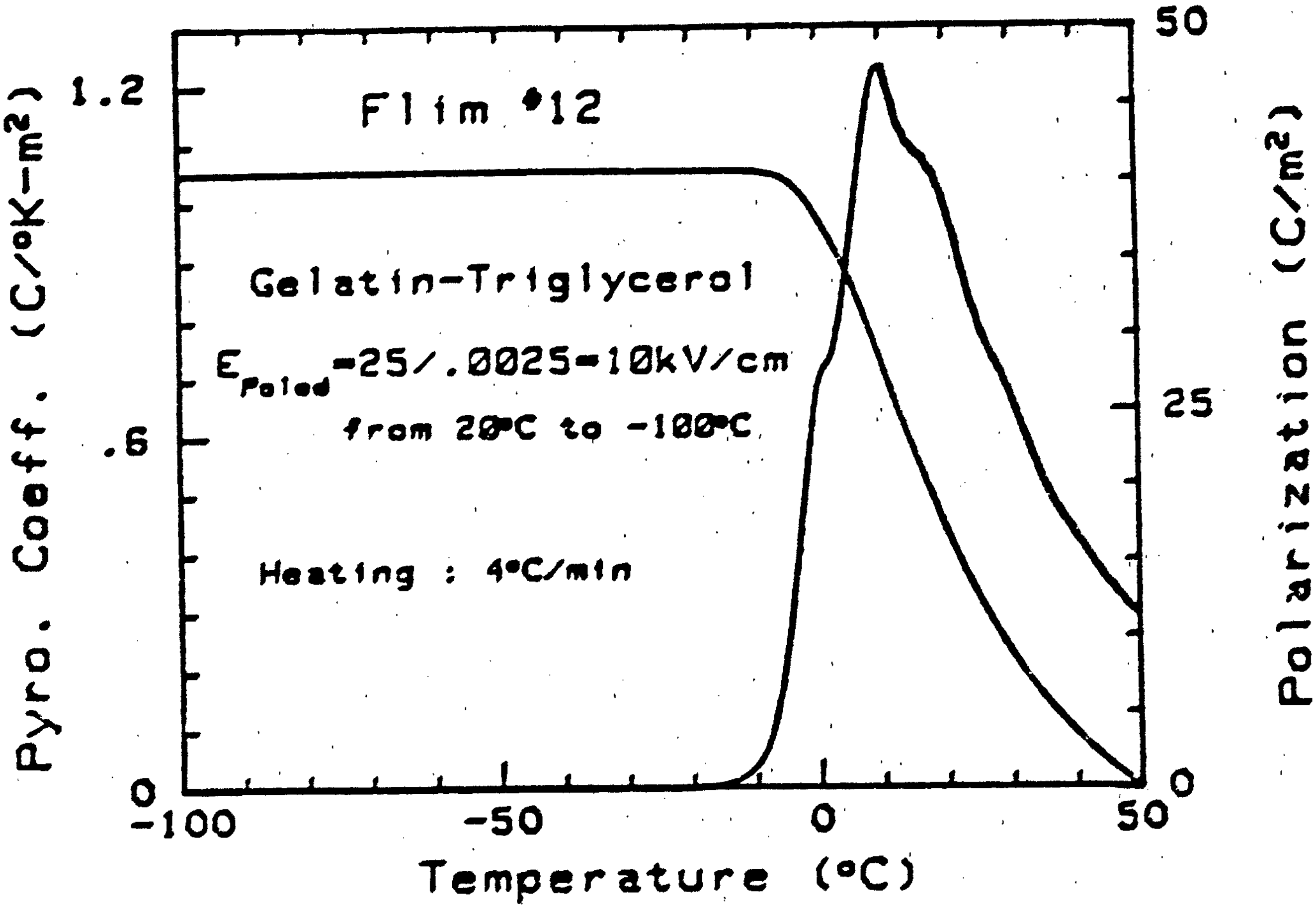
Byer-Roundy measurement of the pyroelectric coefficient and integrated polarization charge in 4- nitrobenzaldehyde modified gelatin. Heating rate 4°C/min. , poling field 10 kV/cm.

Fig 37



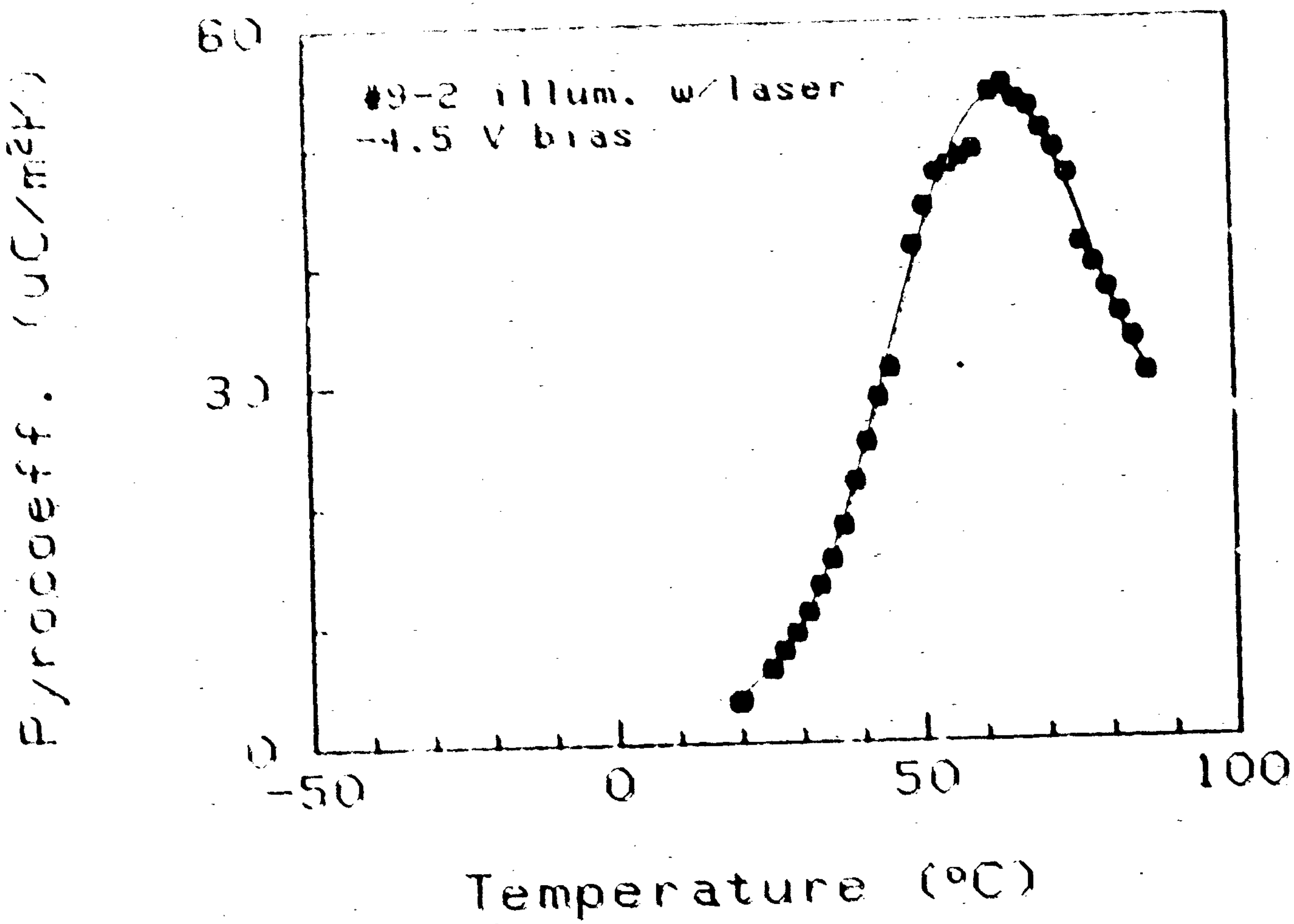
2,4 dinitrobenzaldehyde modified gelatin. Byer-Roundy measurement of the pyroelectric coefficient and of the integrated polarization charge. Heating rate 4°C/min. Poling field 10kV/cm.

Fig 38



Triglycerin modified gelatin. Byer-Roundy measurement of the pyroelectric coefficient and integrated polarization. Heating rate 4°C/min. Poling field 10 kV/cm.

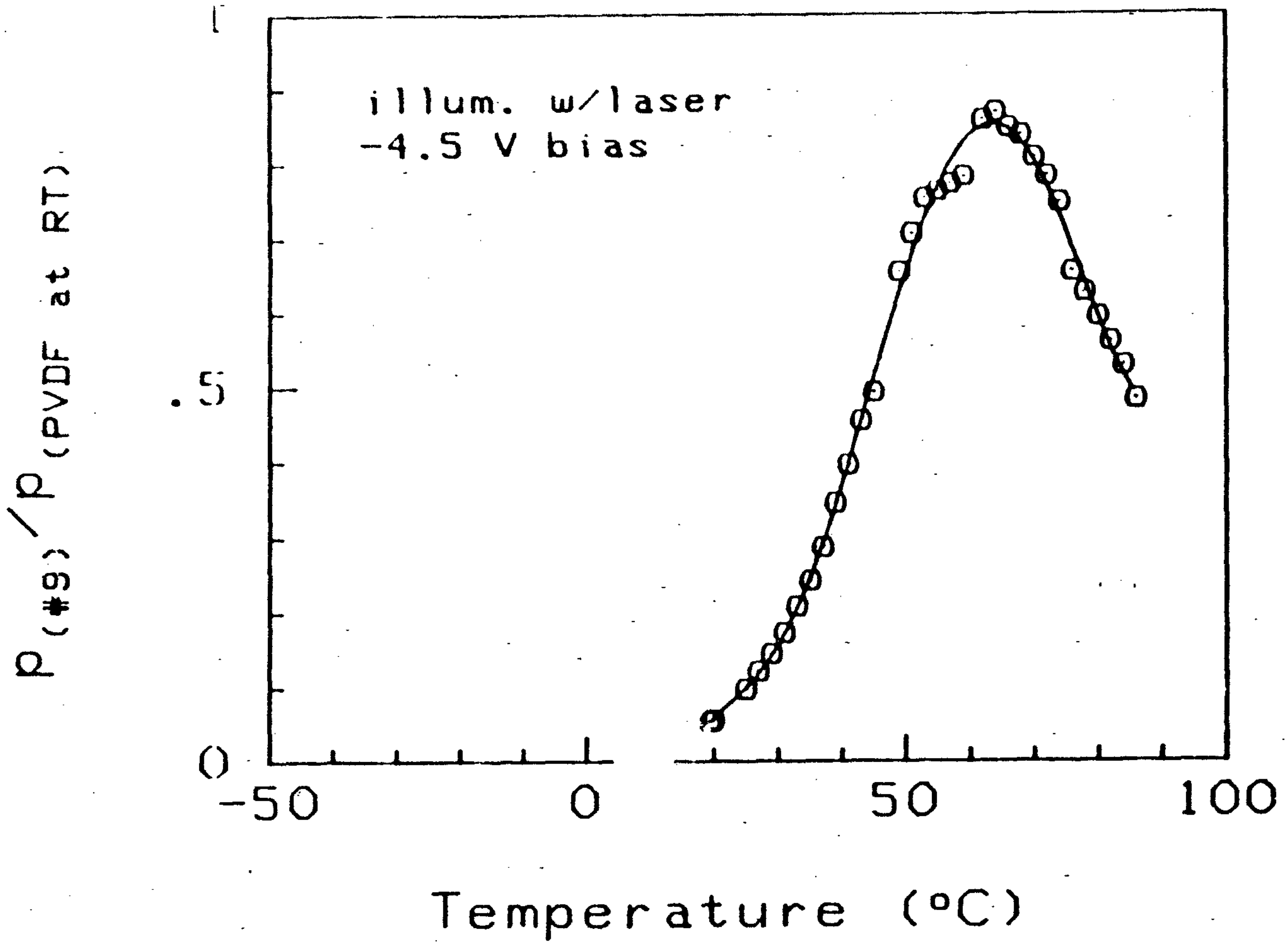
Fig 39



Dec 14, 88.

assumption:
thermal capacity
~2.3·10^6
[illegible]
power ~ 11mW

Fig 40



Dec 14, 88

Assumption
thermal cap$_{\#9}$ =
= thermal cap$_{PVDF}$
= $2.3 \cdot 10^6$ [ ]

Fig41

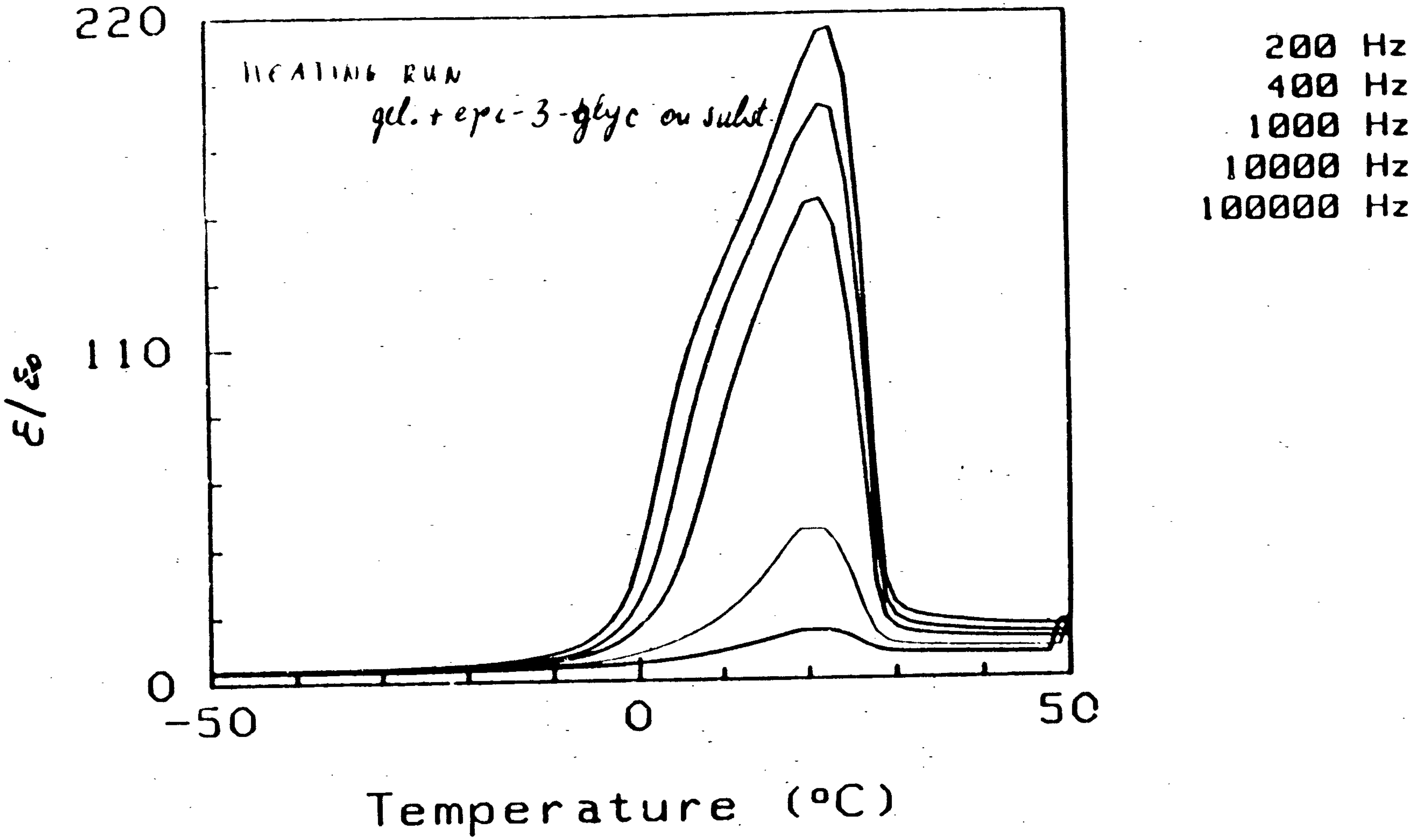

220
110
0
ε/ε0
-50
0
50
Temperature (°C)
HEATING RUN
gel. + epc-3-glyc on subst
200 Hz
400 Hz
1000 Hz
10000 Hz
100000 Hz

Fig 42(a.

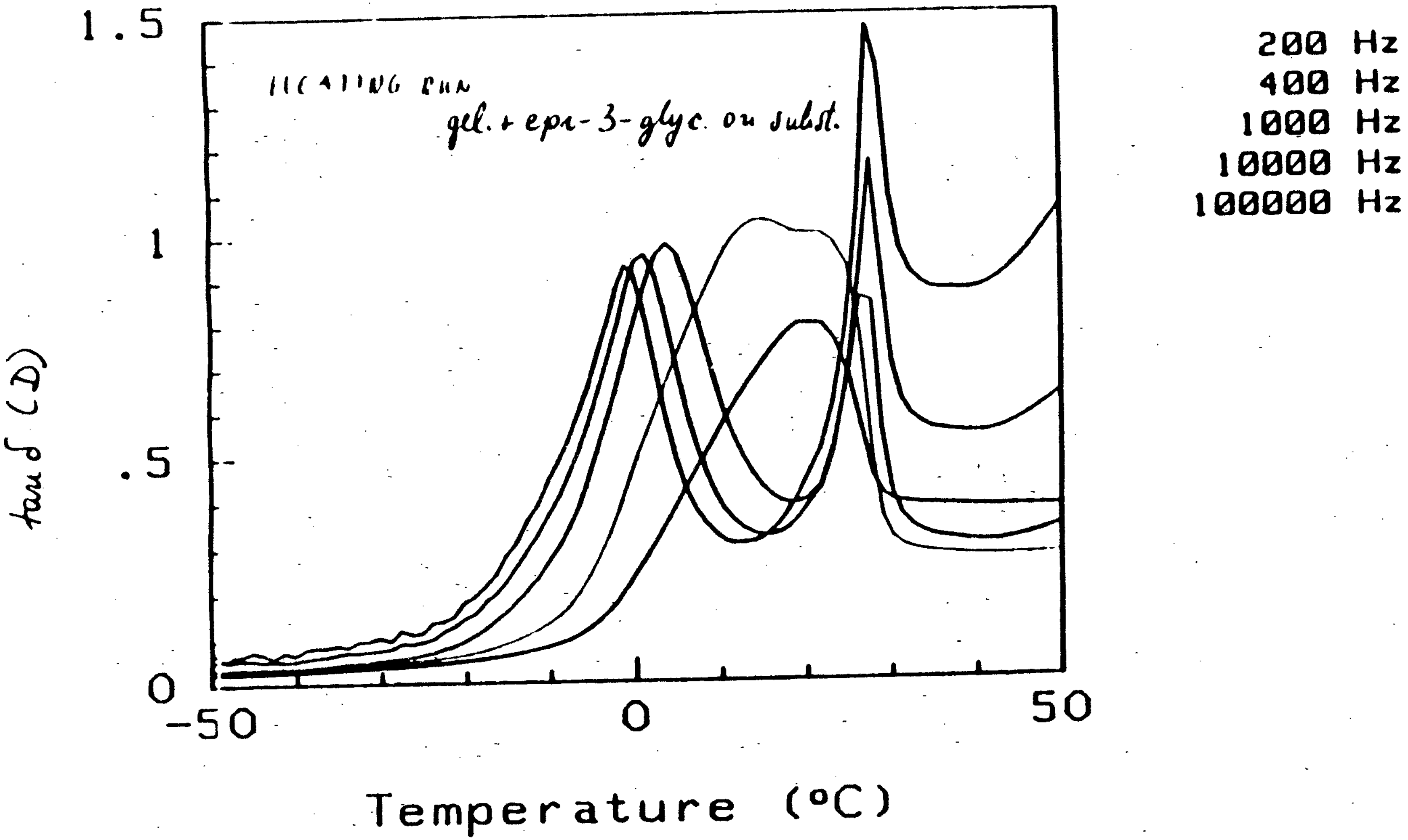

HEATING RUN
gel. + epi-3-glyc. on subst.
200 Hz
400 Hz
1000 Hz
10000 Hz
100000 Hz
1.5
1
.5
0
-50
0
50
tan δ (D)
Temperature (°C)

Fig 42 (b)

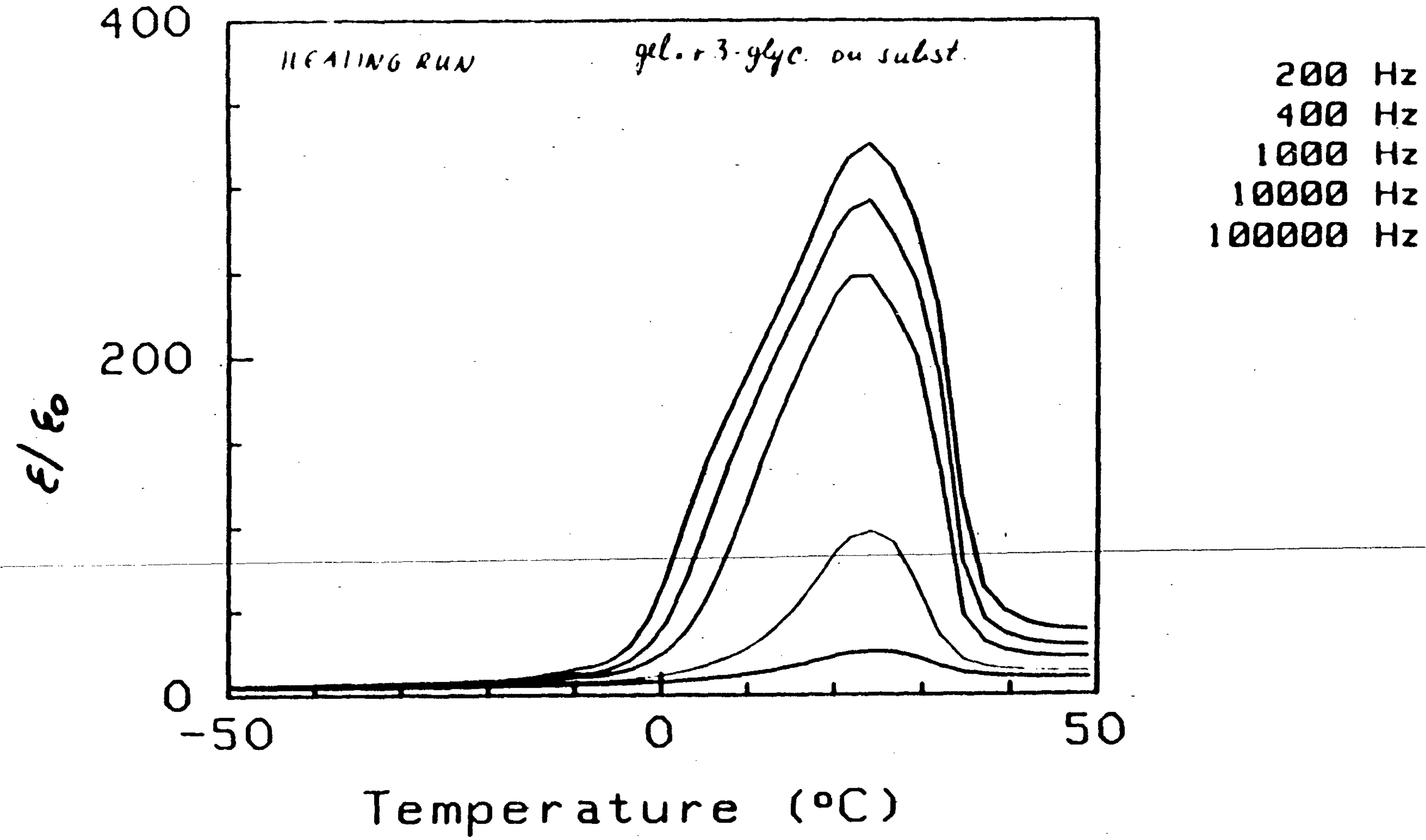

400
200
0
ε/ε0
-50
0
50
Temperature (°C)
HEATING RUN
gel. + 3-glyc. on subst.
200 Hz
400 Hz
1000 Hz
10000 Hz
100000 Hz

Fig 3'a'

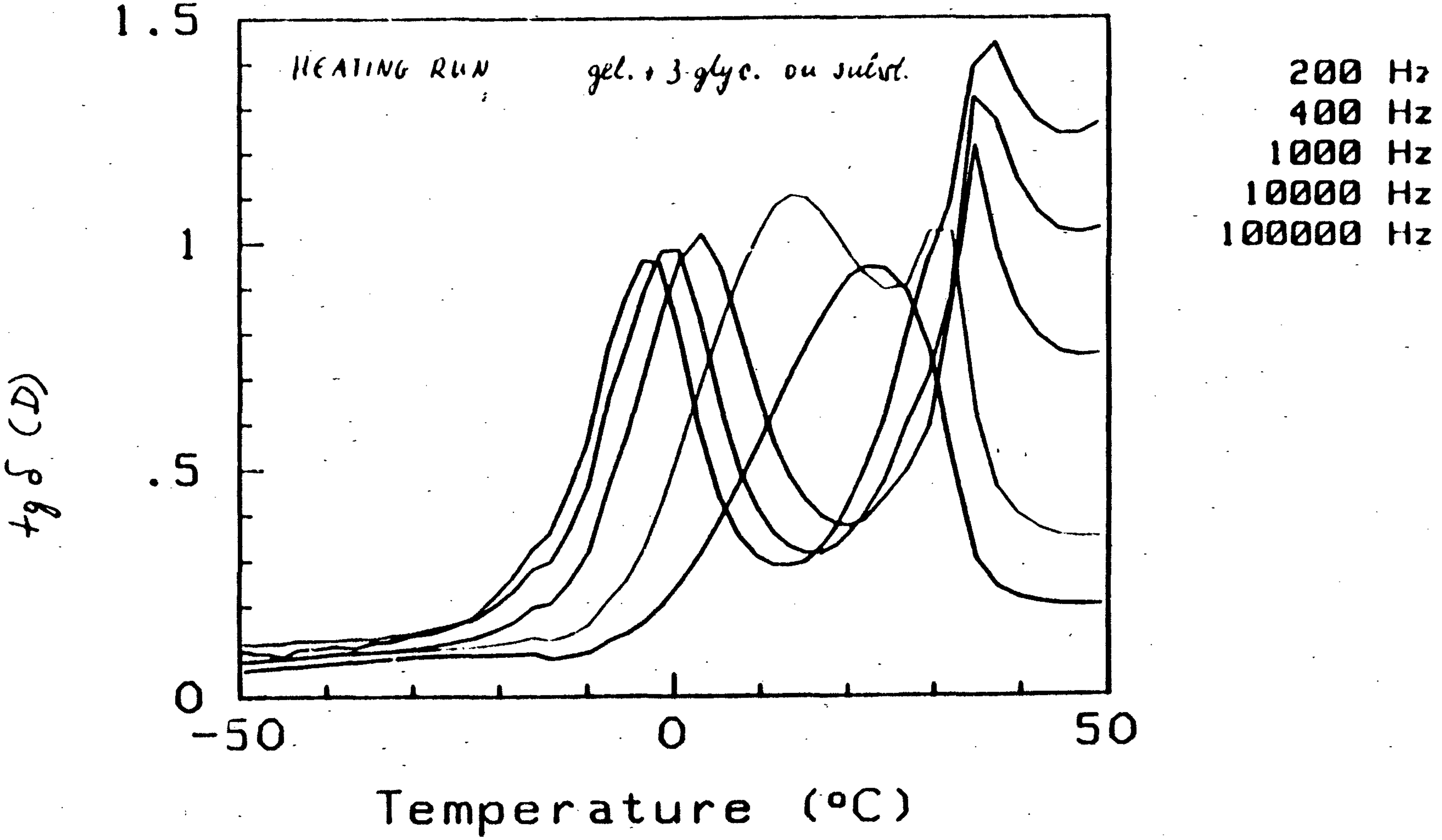

HEATING RUN
gel. + 3 glyc. ou suivt.
1.5
1
.5
0
tg δ (D)
-50
0
50
Temperature (°C)
200 Hz
400 Hz
1000 Hz
10000 Hz
100000 Hz

Fig 13(b)