

AD-A261 505

2



OFFICE OF NAVAL RESEARCH

GRANT # N00014-92-J-1629

R&T Code 4133037---01

DTIC
ELECTE
MAR 4 1993
S C D

Technical Report No. 3

Studies of Water in *Nafion* Membranes:
Dielectric Relaxation and Deuteron and Oxygen-17 NMR

by

R.S. Chen, J.R.P. Jayakody and S.G. Greenbaum, Y.S. Pak,
G. Xu, M.G. McLin and J.J. Fontanella

Prepared for Publication in

Journal of the Electrochemical Society

Hunter College of CUNY
Department of Physics
New York, NY 10021

and

U.S. Naval Academy
Department of Physics
Annapolis, MD 21402-5026

January 25, 1993

Reproduction in whole or in part is permitted for any purpose of the United States Government.

This document has been approved for public release and sale:
its distribution is unlimited.

93-04584



3708

98 1 3 3 060

REPORT DOCUMENTATION PAGE

Form Approved
OMB No 0704-0188

Public domain respondents: this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 25 January 1993	3. REPORT TYPE AND DATES COVERED Interim Technical Report (4/92-	
4. TITLE AND SUBTITLE STUDIES OF WATER IN NAFION MEMBRANES: DIELECTRIC RELAXATION AND DEUTERON AND OXYGEN-17 NMR			5. FUNDING NUMBERS Grant number N00014-92-J-1629	
6. AUTHOR(S) R.S. Chen, J.R.P. Jayakody, S.G. Greenbaum, Y.S. Pak, G. Xu, M.G. McLin and J.J. Fontanella			R&T Code 4133037---01	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Physics Department, Hunter College of CUNY 695 Park Ave., New York, NY 10021; and Physics Department, US Naval Academy Annapolis, MD 21402-5026			8. PERFORMING ORGANIZATION REPORT NUMBER 3	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research, Chemistry Division 800 N. Quincy Street, Arlington, VA 22217-5660			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Accepted for publication in the Journal of the Electrochemical Society				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release and sale; distribution unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Dielectric relaxation and both deuterium and oxygen-17 nuclear magnetic resonance measurements on NAFION-117 membranes with variable water content (~5-18% by weight) are reported. Glassy behavior of the water domains at low T (below ~200 K) is evidenced by the specific nature of the observed dielectric loss peaks and ² H NMR lineshapes. Activation energies extracted from ² H spin-lattice relaxation data on the high T side of the T ₁ minimum exhibit a steady increase with increasing water content. In spite of a high degree of water molecular mobility, angular-dependent spectra in both as-received and stretched samples reflect considerable anisotropy of the host polymer. A dielectric loss peak is observed which has previously been attributed to the glass transition of the aqueous domains.				
14. SUBJECT TERMS NAFION; Deuteron and oxygen-17 NMR; dielectric relaxation; low T properties; anisotropic molecular motion			15. NUMBER OF PAGES 35	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT unclassified	20. LIMITATION OF ABSTRACT UL	

**STUDIES OF WATER IN NAFION MEMBRANES:
DIELECTRIC RELAXATION AND DEUTERON AND OXYGEN-17 NMR**

R.S. Chen, J.P. Jayakody and S.G. Greenbaum
Physics Department, Hunter College of CUNY
New York, NY 10021

Y.S. Pak and G. Xu
Materials Science Department, McMaster University
Hamilton, Ontario L8S 4L7

M.G. McLin and J.J. Fontanella
Physics Department, U.S. Naval Academy
Annapolis, MD 21402-5026

DTIC QUALITY INSPECTED 1

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

ABSTRACT

Deuteron and oxygen-17 nuclear magnetic resonance measurements and dielectric relaxation studies of NAFION-117 membranes with variable water content (approximately 5 - 18% by weight) have been carried out. Glassy behavior of the water domains at low temperature, below about 200K, is evidenced by the specific nature of the ^2H NMR lineshapes. Activation energies extracted from ^2H spin-lattice relaxation data on the high temperature side of the T_1 minimum exhibit a steady increase with increasing water content. In spite of a high degree of molecular mobility, angular-dependent spectra in both as-received and stretched samples reflect considerable anisotropy of the host polymer. A dielectric loss peak is observed which has previously been attributed to the glass transition of the aqueous domains.

Introduction

Perfluorosulfonic acid ionomer membranes are currently receiving a great deal of attention with regard to their ion exchange properties, especially in the context of applications such as fuel cells.¹ Much of the work in the literature concerns the commercial preparation NAFION, which is available in acid or various salt forms. NAFION films readily incorporate water (up to 25% by weight) whose presence greatly facilitates ion transport. A number of studies have been directed at examining the specific role that water plays in proton transport, and related work has addressed the degree of water molecular diffusion through NAFION membranes.²⁻⁴

The physical nature of water in NAFION has been characterized by several techniques and found to be significantly different than in the bulk state. Infra-red spectroscopy indicates the existence of two water environments, which have been postulated as being associated with a void volume and an ion cluster region.⁵ Low temperature ¹H nuclear magnetic resonance (NMR) relaxation time measurements are consistent with glass formation of the water volume.⁶ In addition, recent differential scanning calorimetry (DSC) results for NAFION show glass transitions at about 180 and 210K.⁷

Deuteron NMR has been shown to be a powerful technique in studying structural and dynamical aspects of polymers,⁸ owing to its selectivity (i.e. only the deuteriated portions of the polymer are observed spectroscopically) and the nuclear quadrupole moment of the deuteron, which produces information-rich spectral and relaxation features. It is the latter advantage, of course, that is exploited in this work because the polymer is perfluorinated. This investigation consists of deuteron NMR measurements on NAFION-117 films treated in D₂O in combination with dielectric relaxation (DR) studies. The NMR measurements

were performed as a function of water content in order to examine the effect of water concentration on proton (deuteron) or water molecular mobility. The DR measurements were carried out on NAFION samples containing three different concentrations of water. Supplementary information obtained from DSC and ^{17}O NMR measurements (the latter on films treated with 20% enriched H_2^{17}O) are included.

Both sets of measurements are carried out at low temperatures. In the case of DR, extension to low temperatures makes it possible to study relaxation at audio frequencies. In addition, the NMR T_1 minimum also occurs at low temperatures. These results are of fundamental interest because the low temperature behavior sheds light on the interaction between water molecules and the host polymer. In particular, an important goal is to obtain an improved understanding of the departure of the behavior of water in NAFION from that of bulk water. Finally, it is clear that NAFION is another candidate for low temperature electrochemistry studies as pioneered by Stimming and co-workers with other solid electrolyte systems.⁹

Experimental

Samples of NAFION 117 were obtained from E. I. du Pont Co. For NMR measurements, the NAFION film was cut into parallel strips which were stacked and placed in an open-ended 7mm o.d. NMR tube. The sample was then treated in D_2O (or 20% H_2^{17}O) vapor in a sealed bottle for several days, with various water contents of the NAFION being achieved by adjusting the relative humidity in the bottle through suitable choices of saturated salt solutions. Stretched NAFION samples were prepared by gradually (over a period of several minutes) increasing the tension of a film clamped at both ends, to a maximum elongation of about

120%, and maintaining this position for two days. The tension was then increased until an additional 10-15% elongation was achieved, and the sample was clamped in this position for 4 days. The films were then released and were found to relax to about 115% of the original length after 1 or two days, maintaining this length for about 1 week before further contraction was observed. Moistened films, being less brittle than dry films, were utilized. The stretched film was then dried under vacuum at room temperature and treated in the same manner as the unstretched samples. Deuteron and oxygen-17 NMR data were obtained at a field of 7 T with a Novex NMR spectrometer interfaced to a LeCroy 9400 digital oscilloscope and a microcomputer. Both single-pulse and quadrupole-echo sequences were employed, the latter primarily for measurements of broad spectra at low temperature. Deuteron spin-lattice relaxation times (T_1) were measured by inversion recovery. Recovery profiles were observed to be exponential from room temperature down to about 190K. Some NMR relaxation data at a field of 11.7 T were taken on a Bruker AM-500 spectrometer. Variable temperature control (± 2 K) was achieved by regulating the flow rate of nitrogen gas through a copper heat exchanger.

For the DR measurements, studies were carried out on as-received samples, samples which had been dried in vacuum at about 340K and those which had been soaked in distilled water for several days. Before loading into the sample holder, the as-received sample contained about 4% water by weight relative to the dried sample and the soaked sample contained about 20%. However, because of various procedures discussed below, this does not represent the water content of the samples during the data acquisition. For example, gold electrodes were sputtered onto the surfaces in a two-terminal configuration. Complex impedance measurements were then carried out using a CGA-82 microprocessor controlled bridge which operates at seventeen frequencies

between 10 and 10^5 Hz. Temperatures over the range 5-250K were carried out in a precision Cryogenics CT-14 dewar controlled by a Lake Shore Cryotronics DRC-82 temperature controller using a silicon diode. Further experimental details are given elsewhere.¹⁰

For both sputtering and measurement, the samples were in vacuum and thus water was lost during the procedures. In both cases the time in vacuum at room temperature was minimized. For example, the samples were cooled to 5K as quickly as possible and the low temperature measurements were carried out first. In addition, during loading the as-received and wet samples were exposed to the atmosphere. While most of the loading of the dried sample was done in a dry box, it too was exposed to atmosphere for a short time. Consequently, the dried sample had some opportunity to take up water.

The resultant values of the capacitance, C, and the conductance divided by the angular frequency, G/ω , were then transformed to the the apparent complex dielectric constant, $\epsilon^* = \epsilon' - j\epsilon''$, by determining the area, A, and the thickness, d, of the sample and calculating the value of the real part of the dielectric constant, ϵ' , at room temperature. It was then assumed that the relative change in the real part of the dielectric constant with both frequency and temperature is equal to the relative change in capacitance. The imaginary part of the dielectric constant at all frequencies and temperatures was then calculated using the definition:

$$\epsilon'' = \epsilon' G / \omega C \quad (1)$$

where ω is the angular frequency. It is noted that the electrical conductivity, σ , is related to ϵ'' via:

$$\sigma = \epsilon_0 \epsilon'' \omega \quad (2)$$

The data were also transformed to the loss tangent:

$$\tan\delta = \epsilon''/\epsilon' \quad (3)$$

and the electric modulus which is defined as:

$$M^* = 1/\epsilon^* = M' + jM'' \quad (4)$$

Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments, Inc. Model 2100 DSC. The loading of the dried sample was done in a dry box and the other samples were quickly loaded in atmosphere. Consequently, the DSC results are indeed representative of nominally dry, as-received (4%) and wet (20%) samples.

Results and Discussion

The results of the DSC scans are shown in Figures 1-3. As can be seen in Figure 1, the data for the dry sample show only a weak endotherm at about 413K. The data for the as-received sample, which are shown in Figure 2a, show a much stronger endotherm beginning at about 293K. However, the data for the same sample after having been heated to 423K, which are plotted in Figure 2b, appear very similar to that for the dry sample which was shown in Figure 1. The broad endotherm is attributed to water leaving the sample. In fact, the broad endotherm consists of two components. In addition to the 413K component, there appears to be a feature with a minimum at about 373K. This minimum corresponds to the boiling point of bulk water, and the onset of this peak at lower

temperatures is probably analogous to the depression of the freezing point of pure water (a first order transition) in a confined space.¹¹ This latter feature is prominent in the wet (20 wt%) sample as can be seen in Figure 3a. In the wet sample, there is also an endotherm beginning at about 253K which is attributed to the melting of water in the sample. Again, as is apparent from Figure 3b, the sample exhibits characteristics similar to that for the dry sample after it is heated to 423K.

Despite extensive searching, features at 180K and 210K similar to those reported by Uosaki et al.⁷ were not observed. The reason for the difference is not completely clear, however it should be pointed out that in contrast with the samples studied in the present work, the materials studied by Uosaki et al.⁷ were saturated with a 0.5 M H₂SO₄ solution.

Deuteron NMR linewidths of D₂O-containing NAFION film rolled into a cylinder (to suppress anisotropies which will be discussed later) as a function of water content at 295K are displayed in Figure 4a. As water content is increased the linewidth decreases, approaching the spectrometer limit of 30 Hz as the film becomes saturated. D₂O concentration-dependent spin-lattice relaxation times (T₁) at 295K are shown in Figure 4b. The T₁ values exhibit an approximately linear increase with increasing water content, approaching the value for free D₂O (approximately 400 ms).¹² The data in Figures 4a and 4b are consistent with the expectation that at least some fraction of the total water in the film will approach an isotropically free state, and that rapid exchange, on the NMR timescale, between these nearly free water molecules and those that are more motionally restricted (by interaction with the polymer host) will yield an averaged response. Such behavior is commonly observed in organic membranes containing large amounts (≥ 10 wt%) of water.¹³

Arrhenius plots of deuteron T_1 in NAFION at four different water concentrations (4.7, 10, 14 and 18%) are shown in Figure 5a. All samples exhibit a T_1 minimum at about 205K. Activation energies for deuteron motion have been extracted from the high T (with respect to the T_1 minimum) data in Figure 5a and are listed in Table 1. In the calculation of activation energy a simple exponential relaxation process was assumed along with the fast motion approximation $\omega\tau_c \ll 1$ as originally proposed by Bloembergen, Purcell & Pound (BPP).¹⁴ This approximation yields

$$(T_1)^{-1} \propto \tau_c = \tau_0 \exp(-E_A/kT) \quad (5)$$

where ω is the NMR frequency, τ_c is the motional correlation time and E_A is the activation energy. Although the true relaxation process is undoubtedly more complex than given by the BPP approximation, the rationale for using Equation (5) is that comparisons are being made between samples in which only one parameter (water content) is varied. Thus it is the relative change in activation energy that is physically significant. From Table 1, it can be seen that E_A increases with increasing water content. It is interesting to note that the values in Table 1 are somewhat larger than the corresponding activation energy for free molecular rotation in liquid D_2O (0.14 eV).¹² This observation is consistent with earlier proton NMR results which suggested that thermally activated motion of water molecules is somewhat impeded by interactions with the host polymer.¹⁵ Figure 5b is an Arrhenius plot of T_1 data taken at 76 MHz (11.7 T) for NAFION containing 5.1 wt% D_2O . From the data it is seen that the T_1 minimum (approximately 214K) moves to higher T at the higher NMR frequency. The previously reported proton NMR T_1 minimum was attributed to a glass transition in the water domains.⁶ The temperature shift in 2H T_1 minimum (about 7-10K) as

a result of changing the NMR frequency by somewhat less than a factor of two seems rather large. By comparison, an estimated temperature shift in the same frequency regime based on an extrapolation of extensive dielectric relaxation data of a glassforming, hydrogen-bonding molecular liquid, glycerol,¹⁶⁻¹⁷ is approximately 4K. Nevertheless, the 76 MHz data on the high temperature side of the T_1 minimum yields an activation energy of 0.17 eV, which is comparable to the value obtained for the 4.7 wt% sample at 46 MHz (7.0 T).

Although a clear glass transition is not evident from the DSC data in Figure 3, glassy behavior at low temperatures can be inferred from the deuteron NMR lineshape. Figure 6 displays spectra for both D_2O ice at 233K and NAFION containing 10 wt% D_2O at 193K. The ice spectrum exhibits the well-known divergences associated with a spin-1 powder pattern.⁸ The NAFION spectrum, while being of comparable width to the ice spectrum, shows no clear divergences. Although averaging due to molecular motion is partly responsible for this effect, the NAFION lineshape is also attributed to a glassy arrangement of water molecules, in which the associated distribution of deuteron quadrupole coupling parameters smears out the divergences.

Deuteron NMR spectra of an oriented stack of NAFION films containing 8 wt% D_2O at 295K and at several angles between the film plane and the static magnetic field are displayed in Figure 7a. The observed angular dependence indicates that the deuteron motion, while rapid on the NMR timescale, is anisotropic. That is, although much of the quadrupole interaction is averaged out by molecular motion, residual molecular orientation persists approximately in the plane of the film. Figure 7b shows the angular dependence for a film of 8 wt% D_2O that was stretched by 13%. The largest splitting occurs when the static magnetic field is parallel to the stretch direction. This splitting represents a spectral width nearly a factor of five greater than that of the unstretched film. In

addition the angular dependence follows the $3\cos^2\Theta-1$ dependence of the quadrupole splitting, given that the average principal axis of the electric field gradient (efg) tensor is along the stretch direction.¹³ This conclusion is most evident by observing that the splitting reaches a minimum at the 60° orientation, which is close to the angle at which the quadrupole splitting vanishes (The actual value is 54.7° and the angular positions reported in Figure 7 have an uncertainty of about $\pm 3^\circ$). It is interesting that the 0° spectrum in Figure 8 suggests the presence of two inequivalent deuteron sites in the stretched film. Whether this inequivalence is in fact generated or merely resolved by stretching is not known. Alternatively, the lower intensity inner peaks of the $\Theta=0^\circ$ spectrum may simply be a result of strong orientation, induced by stretching, of the residual efg principal axis.

Finally, ^{17}O NMR spectra of an 8 wt% H_2O film stack (^{17}O enrichment is 20%) are shown in Figure 8a. Because of the considerably larger quadrupole interaction of ^{17}O relative to ^2H (for the same molecule), the spectra are correspondingly broader than in Figure 7. The spectra exhibit one clear set of satellite transitions with an angular dependence similar to that of Figure 8, demonstrating that the efg principal direction (for the ^{17}O quadrupole interaction) is in the plane of the film, more so than the deuteron efg in the unstretched film. Thus both the ^2H and ^{17}O results indicate that residual molecular orientation for unstretched films resides in the plane of the film. This finding is contrary to observations made in cellulose acetate¹³ and polyimide¹⁸ films, in which the residual orientation is perpendicular to the film plane. Of course, the manner in which specific films are processed prior to any manipulations performed in the laboratory, which may include some degree of stretching, will generally have a large effect on the observed anisotropy. Figure 8b displays ^{17}O spectra of a 19%-stretched film containing 16 wt% ^{17}O -enriched H_2O . The resolution of the satellite

transitions and their angular dependence for the relatively modest anisotropy imposed by the 19% elongation are striking. The appearance of only 1 set of quadrupole-split ^{17}O resonances in Figure 8b, as opposed to two sets of ^2H lines in Figure 7b, suggests that site inequivalence explanation of the latter spectrum is unlikely. Thus the ^{17}O NMR result does not confirm the previously referenced IR study which found two different water molecular environments.⁵ However, depending on the timescale of molecular exchange between two inequivalent sites, it is quite plausible for effects observed in IR not to be directly detectable by NMR. Orientation measurements as a function of water content are currently in progress in order to shed additional light on the issue of inequivalent sites.

The results for ϵ' vs. temperature are shown in Figures 9a and 9b. As can be seen in Figure 9a, the results for the "dried" sample exhibit strong dispersion beginning about 175K and are followed by a rapid rise in ϵ' as temperature increases. For the soaked sample, dispersion becomes significant about 25K lower and the onset of a rapid rise in ϵ' as temperature increases also occurs at a lower temperature than for the dried sample. The results for the as-received sample are similar to that for the soaked sample and consequently are not plotted. It is likely that the rapid rise in ϵ' as temperature increases is due to space charge polarization as blocking electrodes have been used. Consequently, the large values of ϵ' observed at high temperatures do not represent a bulk property of the material. Further discussion of such a false contribution to the dielectric constant is given elsewhere.¹⁹

As seen in Figures 10a and 10b, the onset of the rise in the real part of the dielectric constant is accompanied by a rapid increase in the imaginary part of the dielectric constant (and hence electrical conductivity via equation (2)) as temperature increases. The magnitude of ϵ'' is much larger for the soaked sample than for the "dried" sample. This is, of course, due to the ionic

conductivity. In fact, for the 10 Hz data, ϵ'' begins to level out at the highest temperatures. This phenomenon is also apparent in the highest temperature curve at the lowest frequencies in Figure 3 of Starkweather and Chang.¹⁵ This effect, an apparently low conductivity, is another manifestation of blocking electrodes in that the frequency is so low and the mobility is so large that the ions begin to exhibit restricted motion. Further discussion of apparently low values of ϵ'' (and hence electrical conductivity) is given elsewhere.¹⁹

Of most interest for the present work is the shoulder on the low temperature side of the rising conductivity. Specifically, a peak occurs at about 10 Hz and 155K for the wet NAFION and at about 180K for the "dried" material. A similar plot for the as-received NAFION revealed a shoulder at about 10 Hz and 165K. Because of the peak position, it is likely that this relaxation is the same as the relaxation which has been reported by Yeo and Eisenberg²⁰ and Starkweather and Chang¹⁵ both of whom attribute it to the glass transition of the aqueous domains.

The results of the present work are in good agreement with those of Starkweather and Chang.¹⁵ Specifically, they show that "saturated" acid form NAFION should give a 10 Hz water relaxation in the vicinity of 154K as is observed in the present work. It is noted that those authors observed peaks in frequency after subtracting off the background due to the electrical conductivity while in the present work, the peak (shoulder) is observed directly as temperature is varied and no attempt has been made to subtract off the conductivity background. Further, a higher temperature peak, approximately 180K, for samples containing less water is reasonable. For example, Starkweather and Chang¹⁵ show that the temperature of the analogous peak in sodium form NAFION increases as water content decreases.

Yeo and Eisenberg²⁰ also report the variation of peak position with water content though not at 10 Hz. Also, they report their data in terms of $\tan\delta$ (their $\tan\delta_E$). In order to compare results, the data of the present work are replotted using the $\tan\delta$ representation in Figures 11a and 11b. As expected, the results are similar to the ϵ'' representation. However, Yeo and Eisenberg²⁰ do not show a rise in $\tan\delta$ as temperature increases. As is apparent from Figure 11b, a peak is found at high temperature e.g. 225K and 10 Hz for the soaked sample. However, it follows from the results plotted in Figures 9 and 10 that that peak is attributable to blocking electrode effects.

Finally, the imaginary part of the electric modulus is shown in Figures 12a and 12b. As is obvious from the plots, peaks which are reminiscent of standard DR are observed and, in fact, are usually referred to as the conductivity relaxation. Other work by several of the authors concerned with ion conducting polymers and which utilizes the electric modulus representation is given elsewhere.²¹ For NAFION, it is clear that the conductivity relaxation shifts to higher temperature as the water content decreases. For example, the peak at 10 Hz for the soaked sample occurs approximately 40K lower than the 10 Hz peak for the dried sample. This, of course, merely reflects the increasing ionic conductivity but has the advantages of representing conductivity as a peak and suppressing blocking electrode effects.²¹ In order to relate the conductivity relaxation to water content, it will be necessary to better control the water content of the samples during DR measurements. Such experiments are currently underway.

Conclusions

Previous investigations on the nature of water in NAFION have demonstrated significant departures from bulk water behavior. This conclusion is borne out in the present study by examination of low temperature properties, and by spectroscopic results which reflect the underlying anisotropy of the host polymer. Despite the absence of a clear DSC glass transition, dielectric relaxation and the low temperature deuteron NMR lineshape suggest that the water molecules reside in glassy domains. The activation energy corresponding to deuteron spin-lattice relaxation in NAFION increases with increasing water content. Thus even fully saturated films do not exhibit behavior consistent with isotropically free water contained in voids. Finally, despite the highly mobile state of the water molecules at room temperature, residual orientation approximately in the plane of the film is evidenced by both ^2H and ^{17}O spectra. This anisotropy can be enhanced dramatically by modest stretching (less than 20%) of the film.

Acknowledgments

This work was supported in part by the U.S. Office of Naval Research, NSERC and the PSC-CUNY Award Program. The authors would like to thank Walther Grot of DuPont Co. for supplying the NAFION samples.

References

1. S.J. Sondheimer, N.J. Bunce, C.A. Fyfe, *J. Macromol. Sci.-Rev. in Macromol. Chem. and Phys.* **C26**, 353 (1986).
2. R.C.T. Slade, J. Barker, J.H. Strange, *Solid State Ionics* **35**, 11 (1989).
3. T.A. Zawodzinski, Jr., M. Neeman, L.O. Sillerud, S. Gottesfeld, *J. Phys. Chem.* **95**, 6040 (1991)
4. T.F. Fuller, J. Newman, *J. Electrochem. Soc.* **139**, 1332 (1992).
5. M. Falk, *Can. J. Chem.* **58**, 1495 (1980).
6. N.G. Boyle, V.J. McBrierty, D.C. Douglass, *Macromolecules* **16**, 75 (1983).
7. K. Uosaki, K. Okazaki, H. Kita, *J. Electroanal. Chem.* **287**, 163 (1990).
8. L.W. Jelinski, in High-Resolution NMR Spectroscopy of Synthetic Polymers in Bulk, L. Komoroski, ed., VCH Publisher, New York (1986), Ch.10.
9. U. Frese, U. Stimming, *J. Electroanal. Chem.* **198**, 409 (1986); T. H. Huang, E. Davis, U. Frese, U. Stimming, *J. Phys. Chem.* **92**, 6874 (1988).
10. J.J. Fontanella, C.G. Andeen, D. Schuele, *Phys. Rev.* **B6**, 582 (1972).
11. G.K. Rennie and J.J. Clifford, *J. Chem. Soc., Faraday Trans.* **73**, 680 (1977).
12. J.C. Hindman, A.J. Zielen, A. Svirnickas, M. Wood, *J. Chem. Phys.* **74**, 621 (1971).
13. K. Matsumura, K. Hayamizu, T. Nakane, H. Yanagishita, O. Yamamoto, *J. Polym. Sci.: Part B: Polym. Phys.* **26**, 2215 (1988).
14. A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford (1961), Ch. VII.
15. H.W. Starkweather, J.J. Chang, *Macromolecules* **15**, 752 (1982).
16. D.W. Davidson, R.H. Cole, *J. Chem. Phys.* **19**, 1484 (1951).

17. G.E. McDuffie, T.A. Litovitz, J. Chem. Phys. 73, 616 (1962).
18. S.Z. Li, Y.S. Pak, K.J. Adamic, S.G. Greenbaum, B.S. Lim, G. Xu, A.S. Nowick, J. Electrochem. Soc. 139, 662 (1992).
19. M.C. Wintersgill, J. J. Fontanella, in Polymer Electrolyte Reviews-2, eds. J. R. MacCallum, C. A. Vincent, Elsevier Applied Science, 1989, p. 43.
20. S.C. Yeo, A. Eisenberg, J. Appl. Polym. Sci. 21, 875 (1977).
21. J. J. Fontanella, J. J. Wilson, M. K. Smith, M. C. Wintersgill, C. S. Coughlin, P. Mazaud, S. G. Greenbaum, R. L. Siddon, Solid State Ionics 50, 259 (1992).

TABLE 1: Activation Energies From Figure 7.

Water content (wt%)	E_A (ev)
4.7	0.20
5.1	0.17 (from 76 MHz data)
10.2	0.22
14.1	0.25
18.3	0.27

Figure Captions

Figure 1. DSC scan for dry NAFION. The scan rate was 10 K/min.

Figure 2. (a) DSC scan for as-received (4%) NAFION. (b) DSC scan for as-received NAFION which had been heated to 150C. The scan rate was 10 K/min.

Figure 3. (a) DSC scan for wet (20%) NAFION. (b) DSC scan for wet NAFION which had been heated to 150C. The scan rate was 10 K/min.

Figure 4. (a) Deuteron NMR linewidths in NAFION as a function of D₂O content (by weight). (b) Deuteron spin-lattice relaxation times (T₁) as a function of D₂O content. Data taken at 295K.

Figure 5. Arrhenius plots of deuteron T₁ in NAFION. (a) Data for several water contents at 46 MHz Larmor frequency. (b) Data for 5.1 wt% D₂O sample at 76 MHz.

Figure 6. Low T spectra of D₂O ice (233K) and NAFION with 10 wt% D₂O (193K). Only half of the true absorption spectra (which are symmetric) are shown.

Figure 7. Angular variation of deuteron NMR spectra in NAFION containing 8 wt% D₂O at 295K: (a) unstretched film; (b) 13% stretched film. Angle measured between film plane or stretch direction and static magnetic field.

Figure 8. Angular variation of oxygen-17 NMR spectra in NAFION containing 16 wt% H₂O (¹⁷O enrichment is 20%) at 295K: (a) unstretched film; (b) 19% stretched film.

Figure 9. Real part of the dielectric constant vs. temperature at three frequencies for (a) nominally dry and (b) nominally wet NAFION. Straight line segments connect the data points.

Figure 10. Imaginary part of the dielectric constant vs. temperature at three frequencies for (a) nominally dry and (b) nominally wet NAFION. Straight line segments connect the data points.

Figure 11. $\tan\delta$ vs. temperature at three frequencies for (a) nominally dry and (b) nominally wet NAFION. Straight line segments connect the data points.

Figure 12. Electric modulus vs. temperature at three frequencies for (a) nominally dry, (b) nominally wet NAFION. Straight line segments connect the data points.

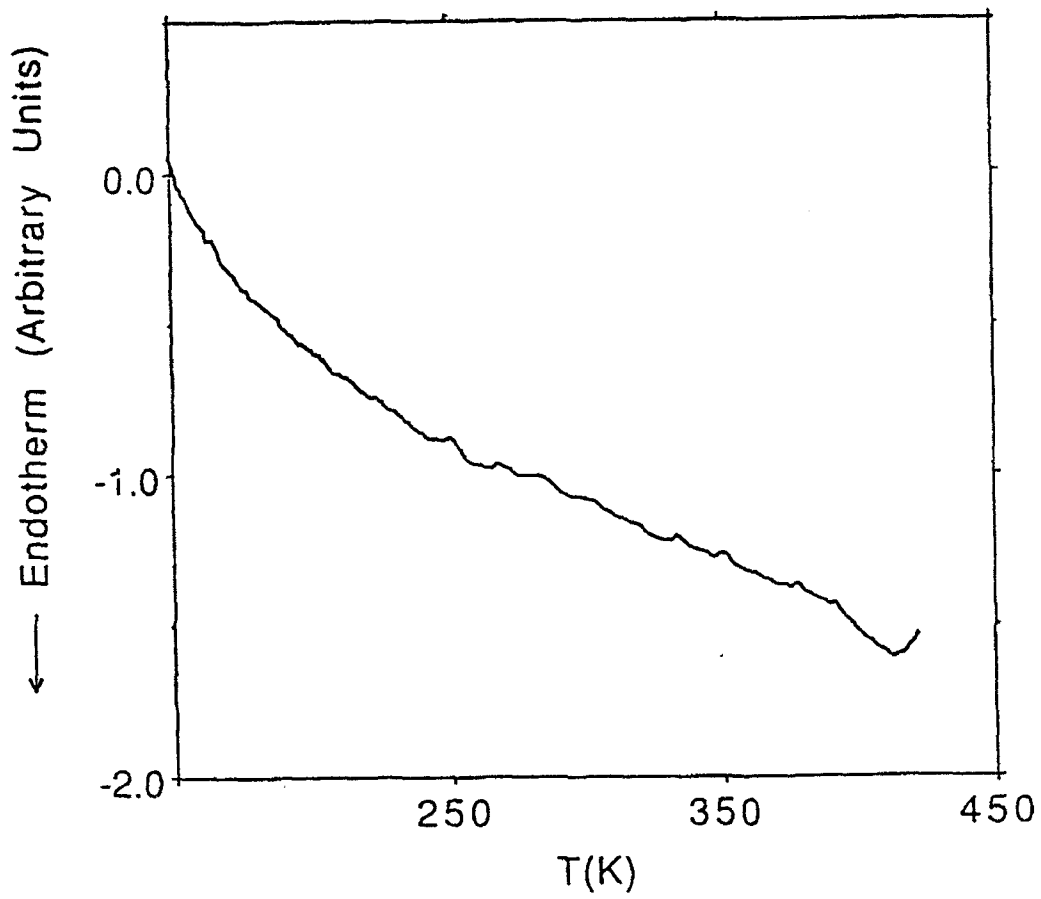


Fig. 1
Chen, et al.

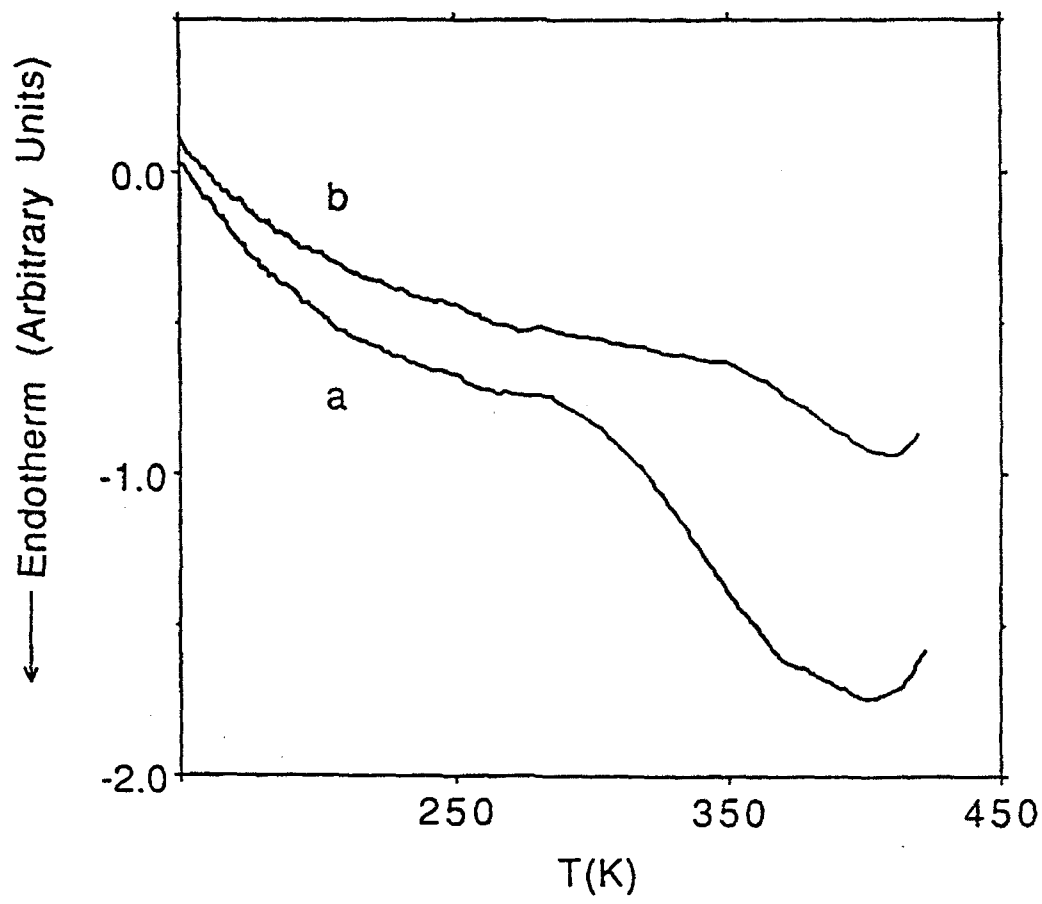


Fig 2
Chen et al.

References

- Barhyte, D. Y., & Glandon, G. L. (1988). Issues in nursing labor costs allocation. Journal of Nursing Administration, 18(12), 16-19.
- Birch & Davis Associates, Inc. (1990). Functional requirements, implementation, and assessment assistance support for worldwide automation initiatives: Relationship of DRGs and nursing workload in the Department of Defense. Contract No: MDA903-88-C-0071. Silver Springs, MD: Author.
- Bost, D., & Lawler, T. G. (1989). Measuring nursing resource consumption. Nursing Management, 20(2), 34-35.
- Caterinicchio, R. P. (1983). A debate: RIMs and the cost of nursing care. Nursing Management, 14(5), 36-39.
- Cromwell, J., & Price, K. F. (1988). The sensitivity of DRG weights to variation in nursing intensity. Nursing Economics, 6(1), 18-26.
- Division of Nursing. (1990, December). Nursing service operating instruction 168-1: Workload system for nurses. Lackland Air Force Base, TX: Wilford Hall Medical Center.

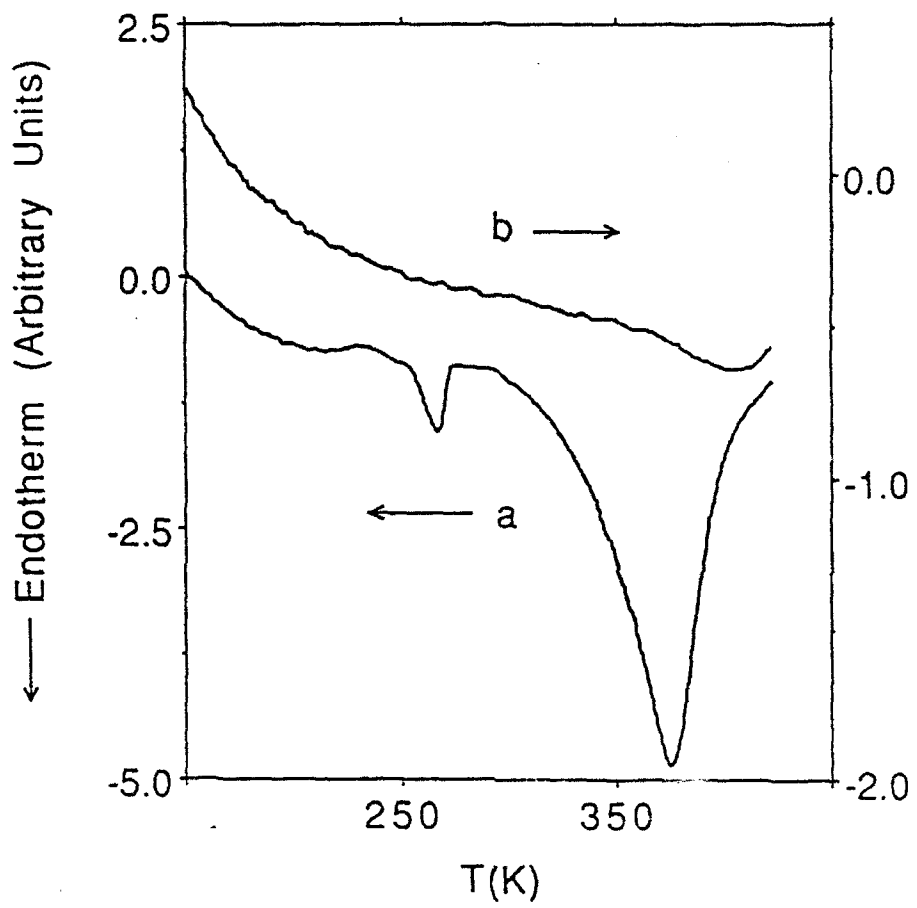
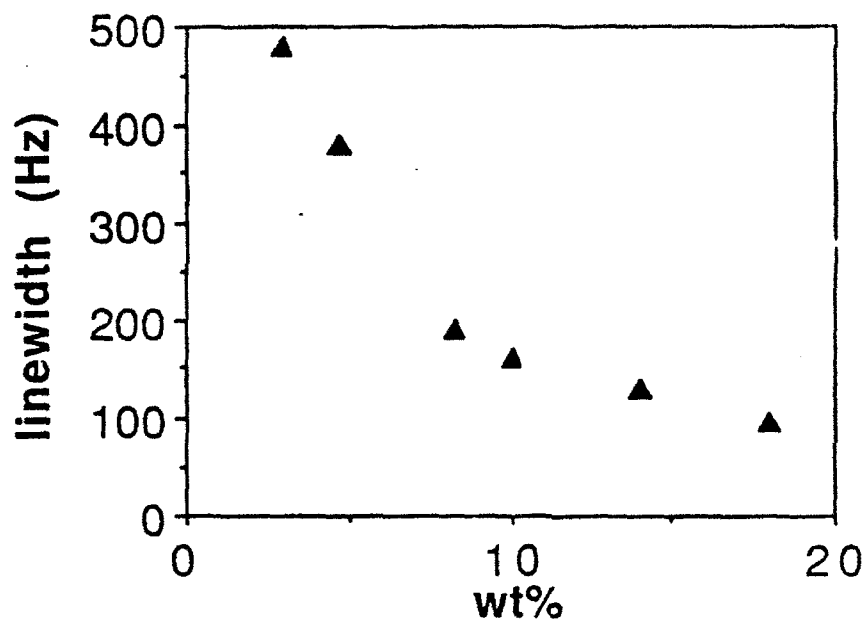
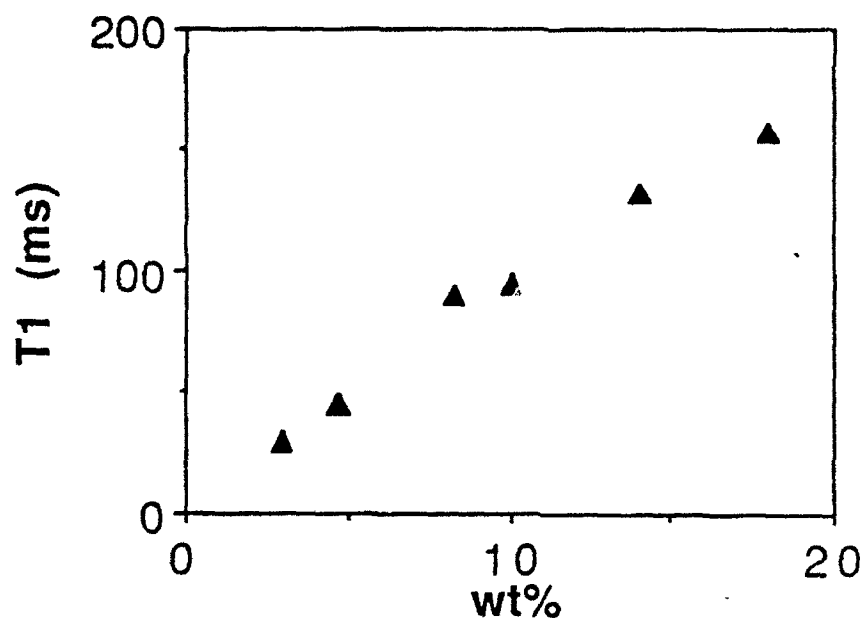


Fig 3
Chen et al



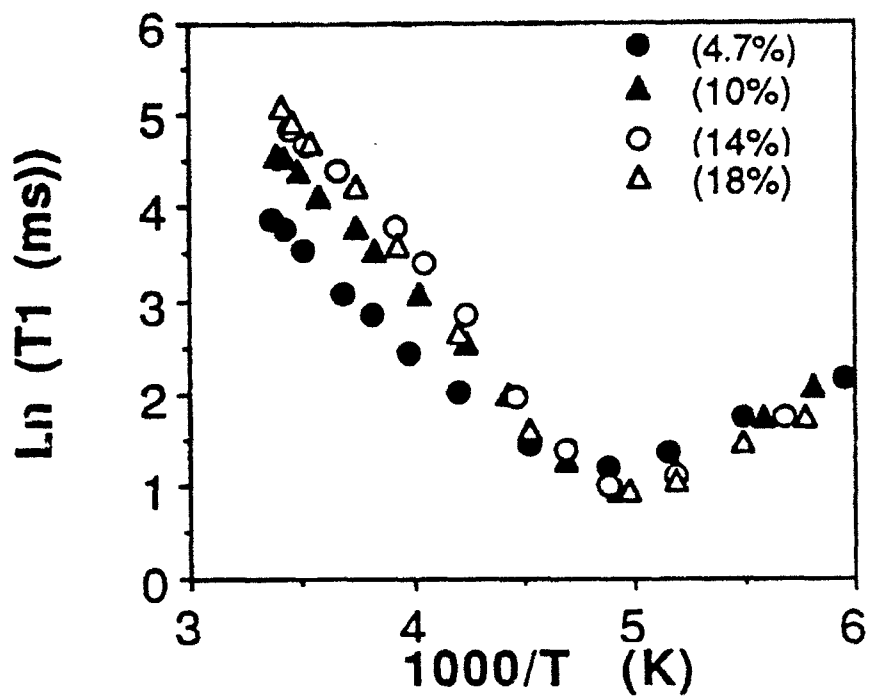
(a)



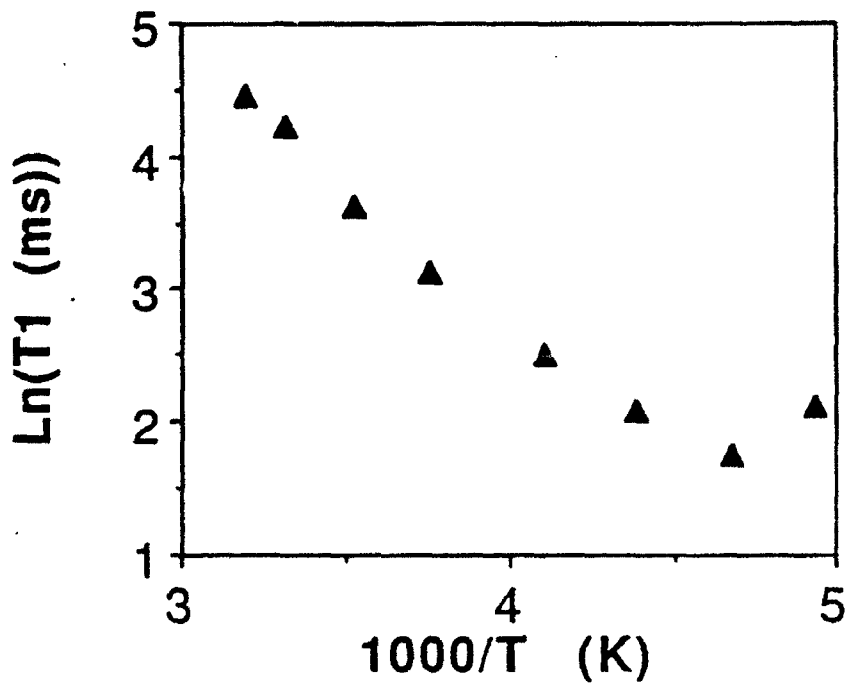
(b)

Fig 4

10/1/13



(a)



(b)

F. E.

1972



(a)



(b)

50 kHz
└────────┘

Fig. 1
Cl. 10/1

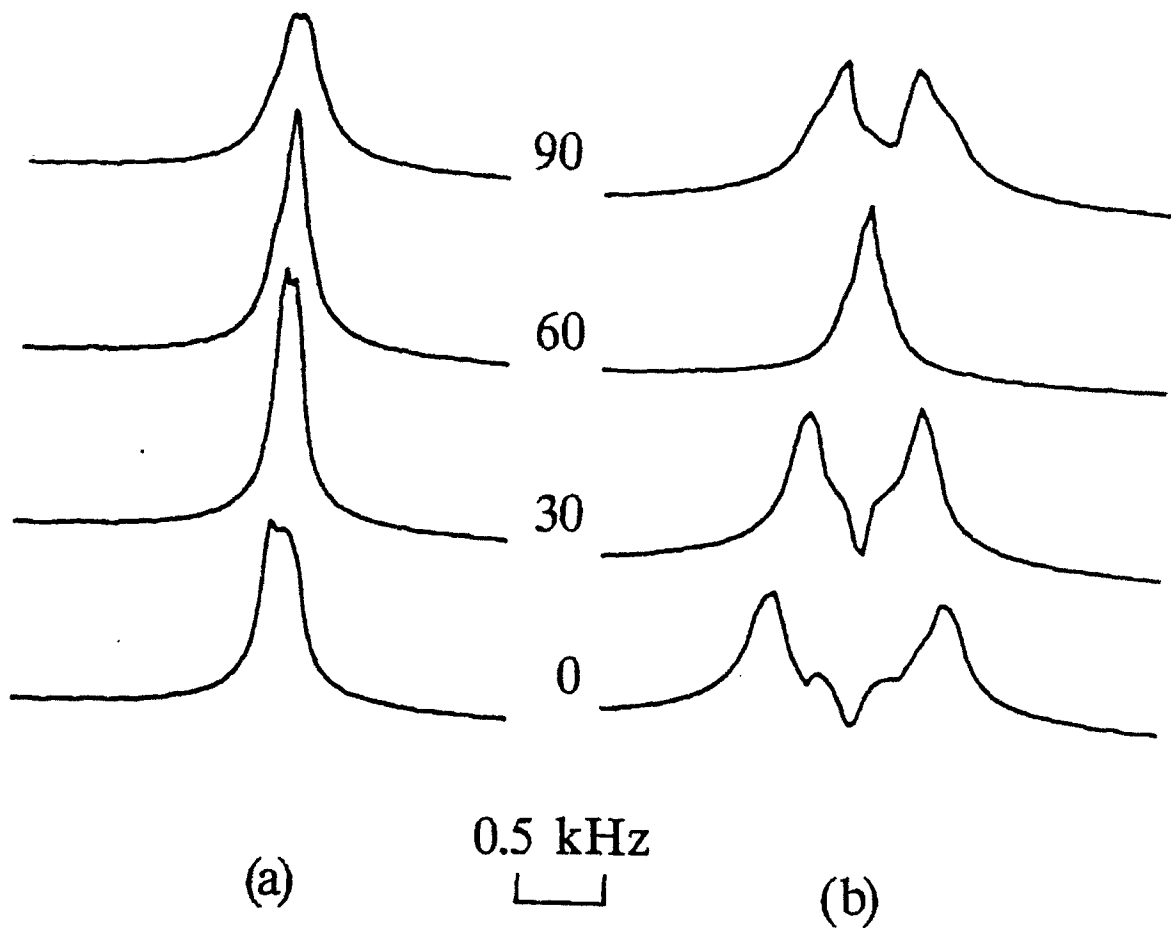
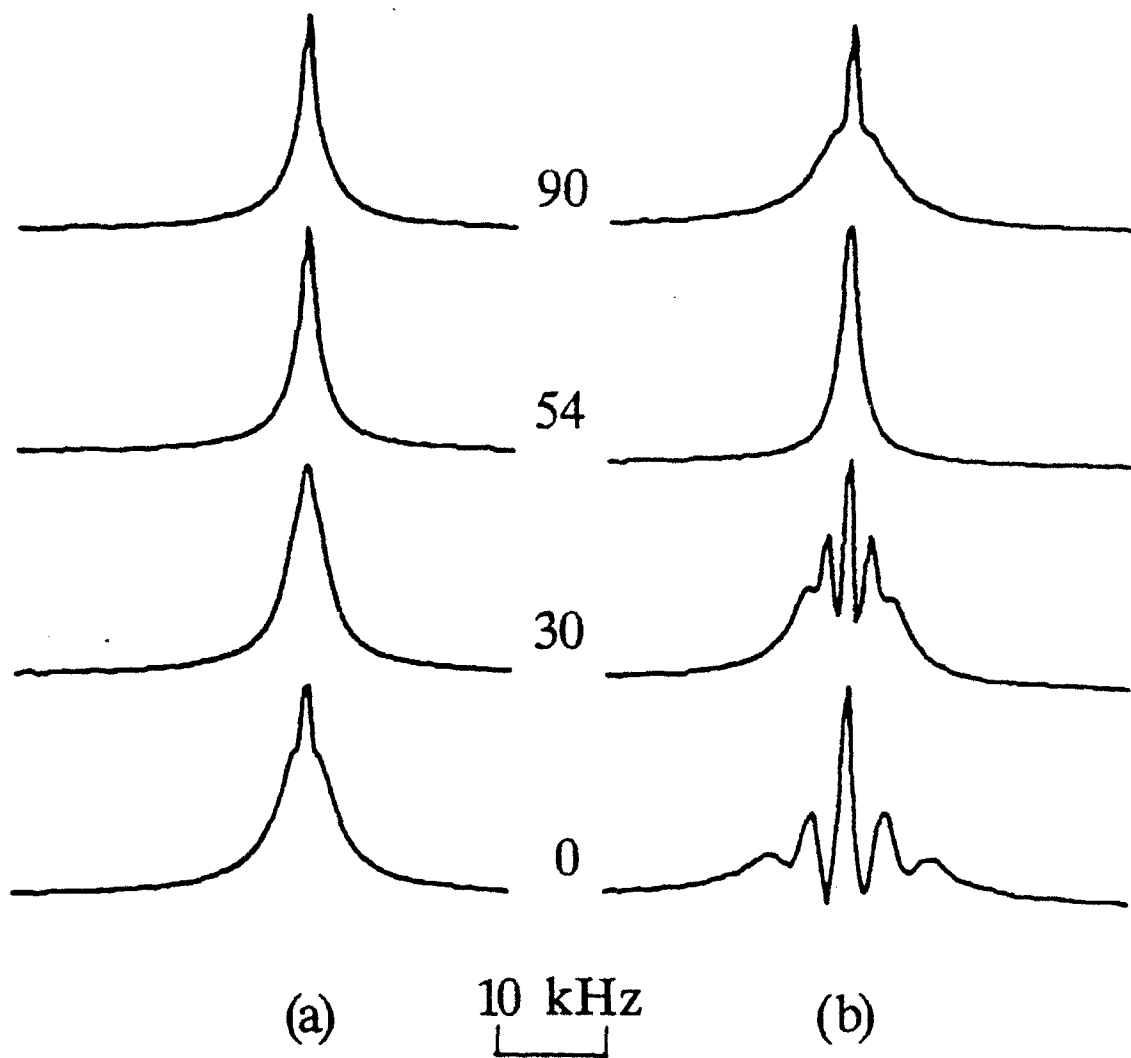


Fig 7



5
30
1

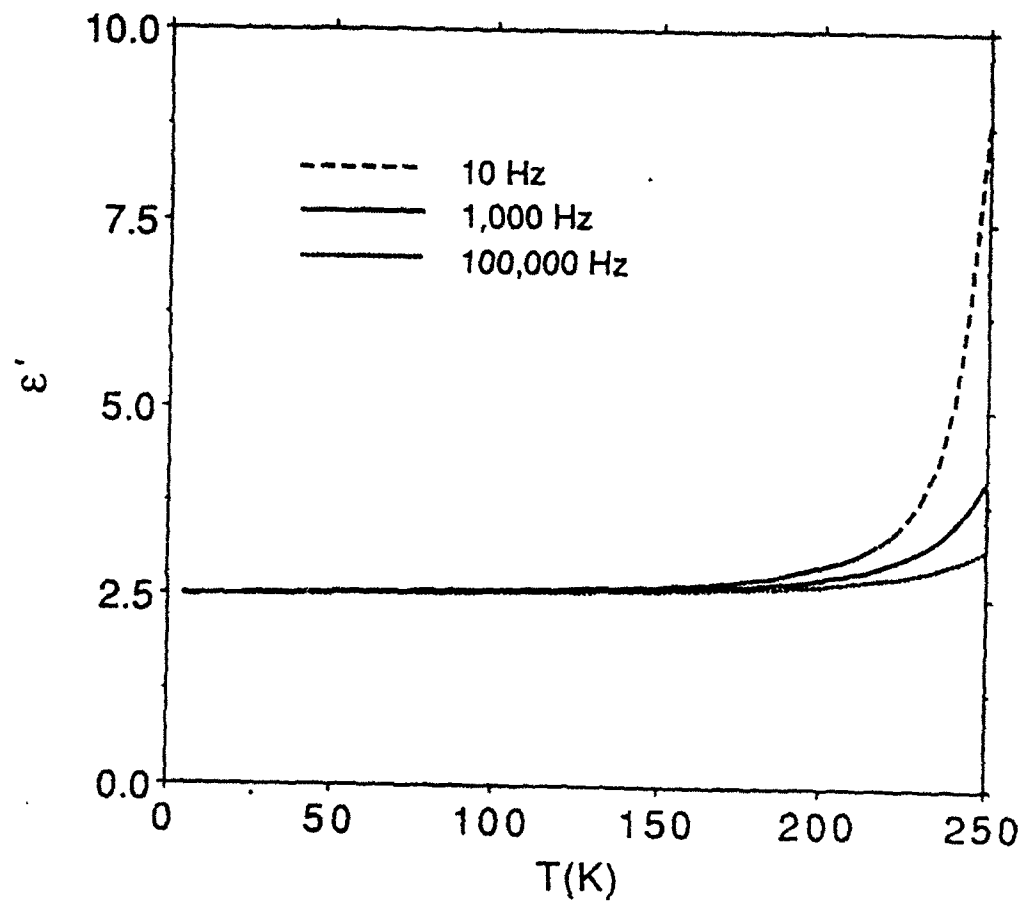
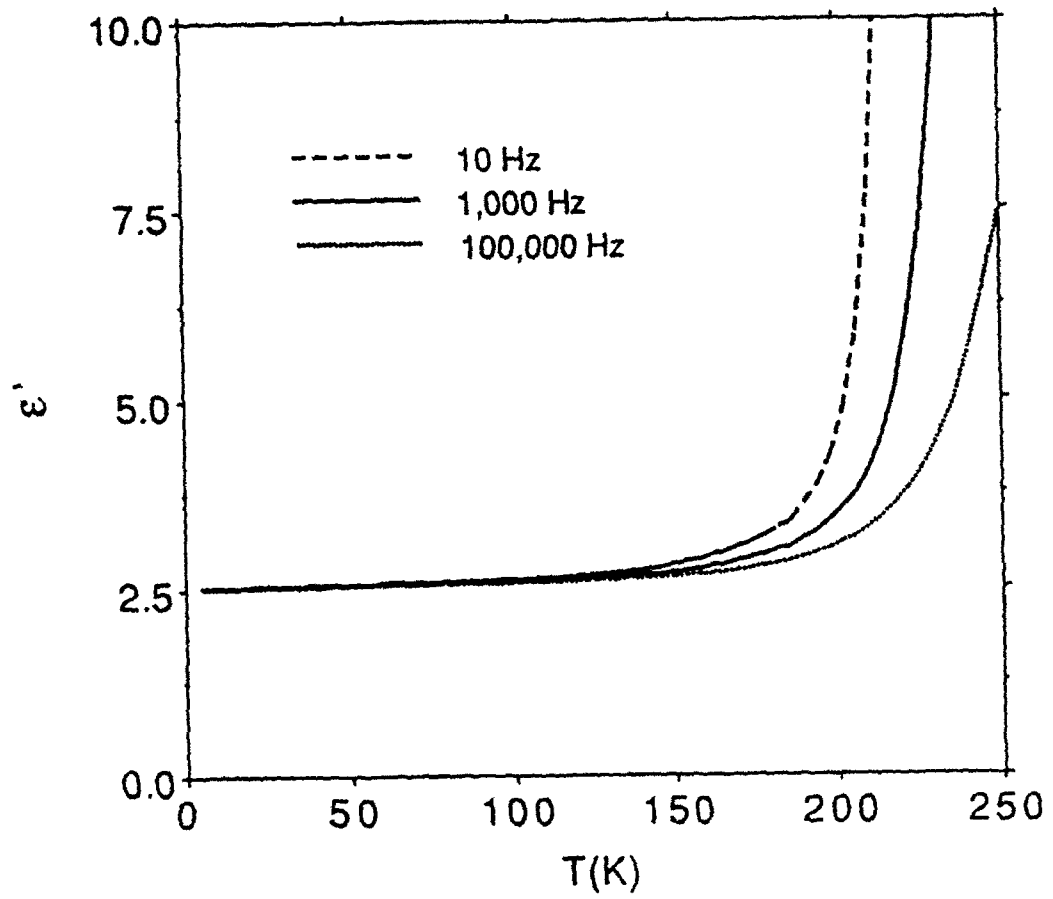
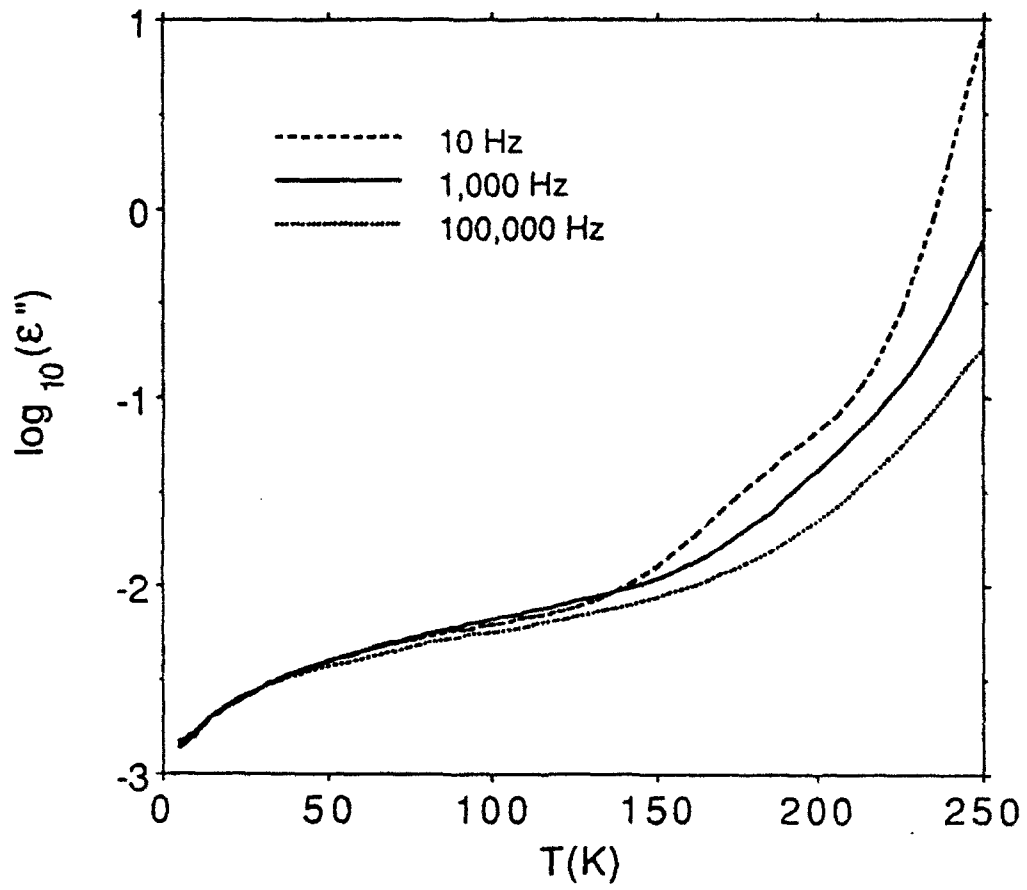


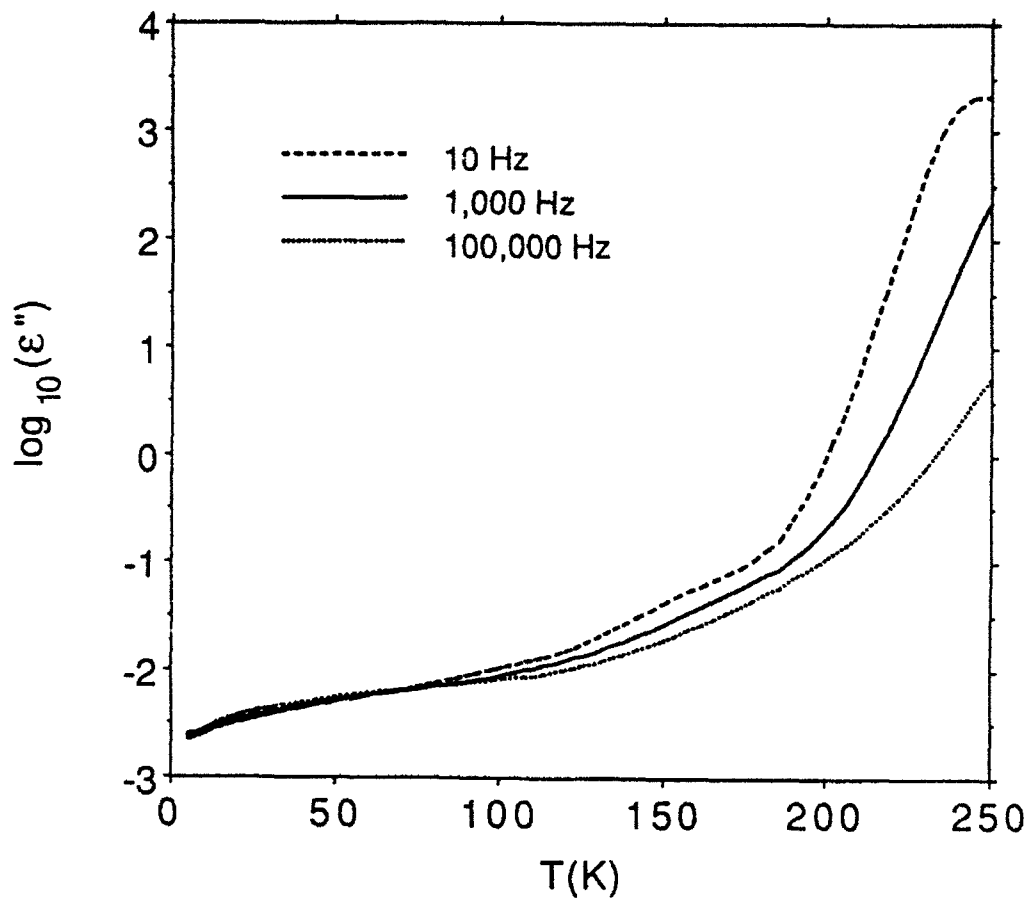
FIG. 1

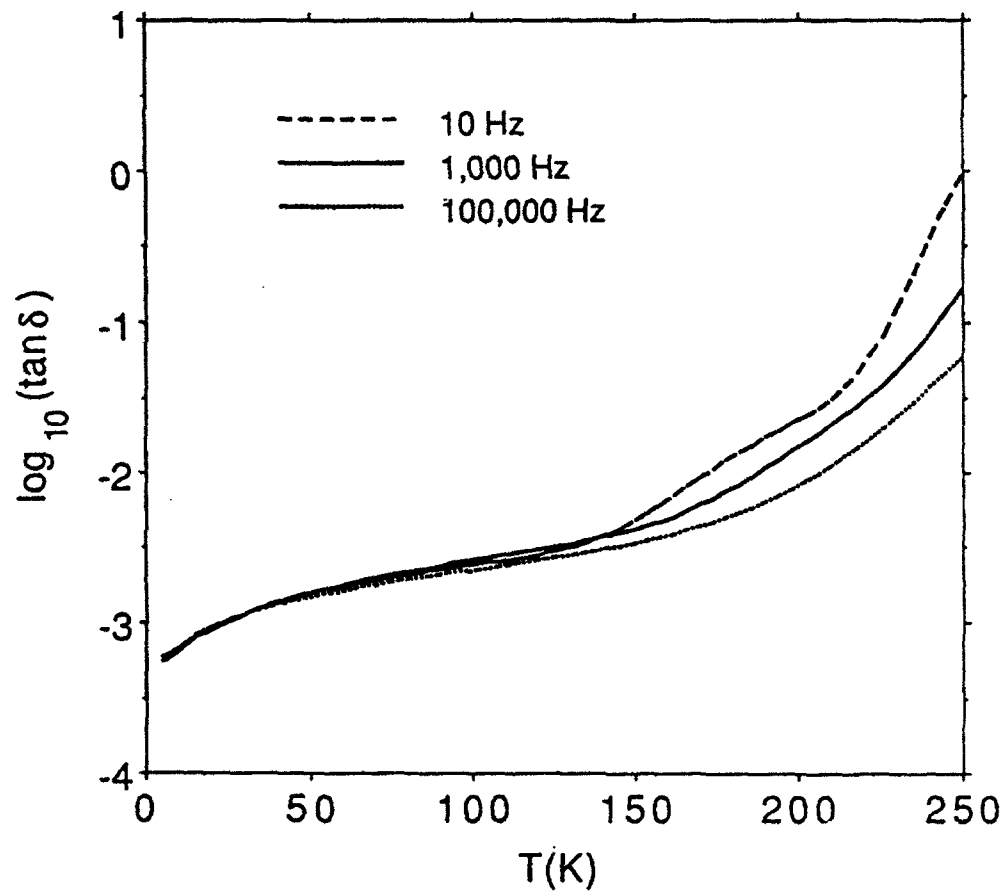


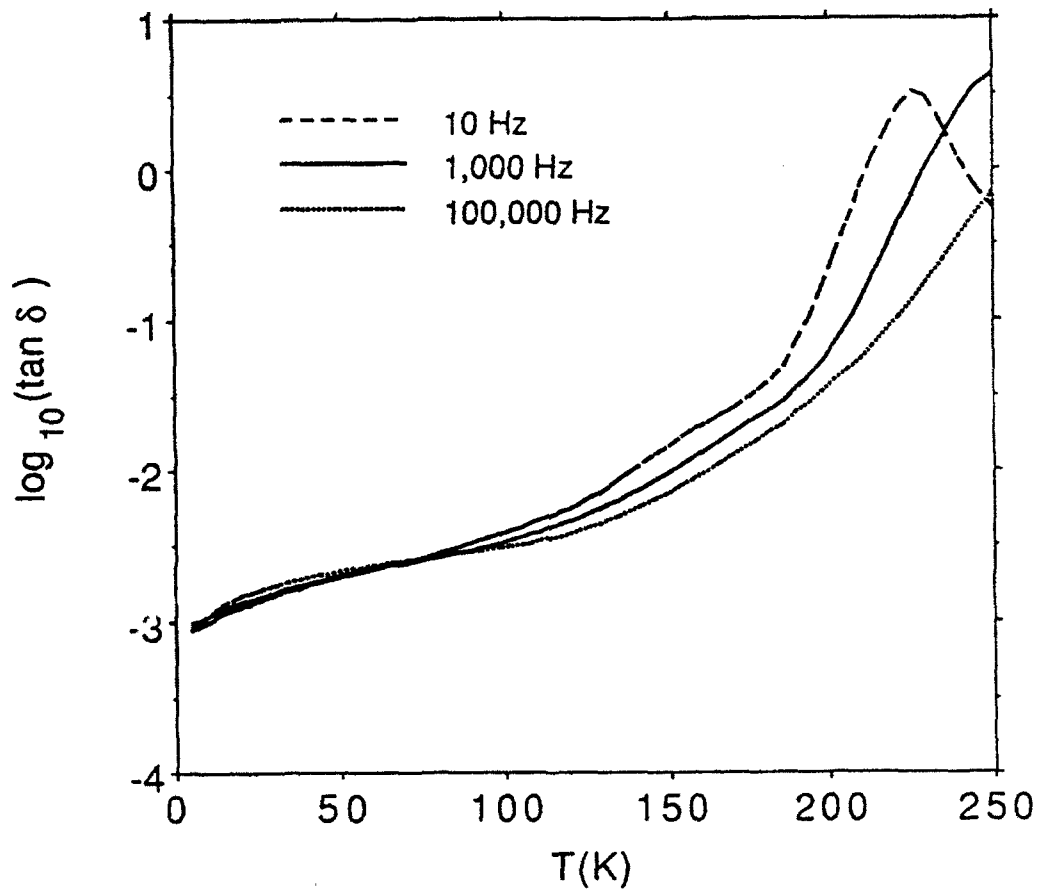
0.0
4.182



Handwritten notes or a signature in the bottom right corner of the page.







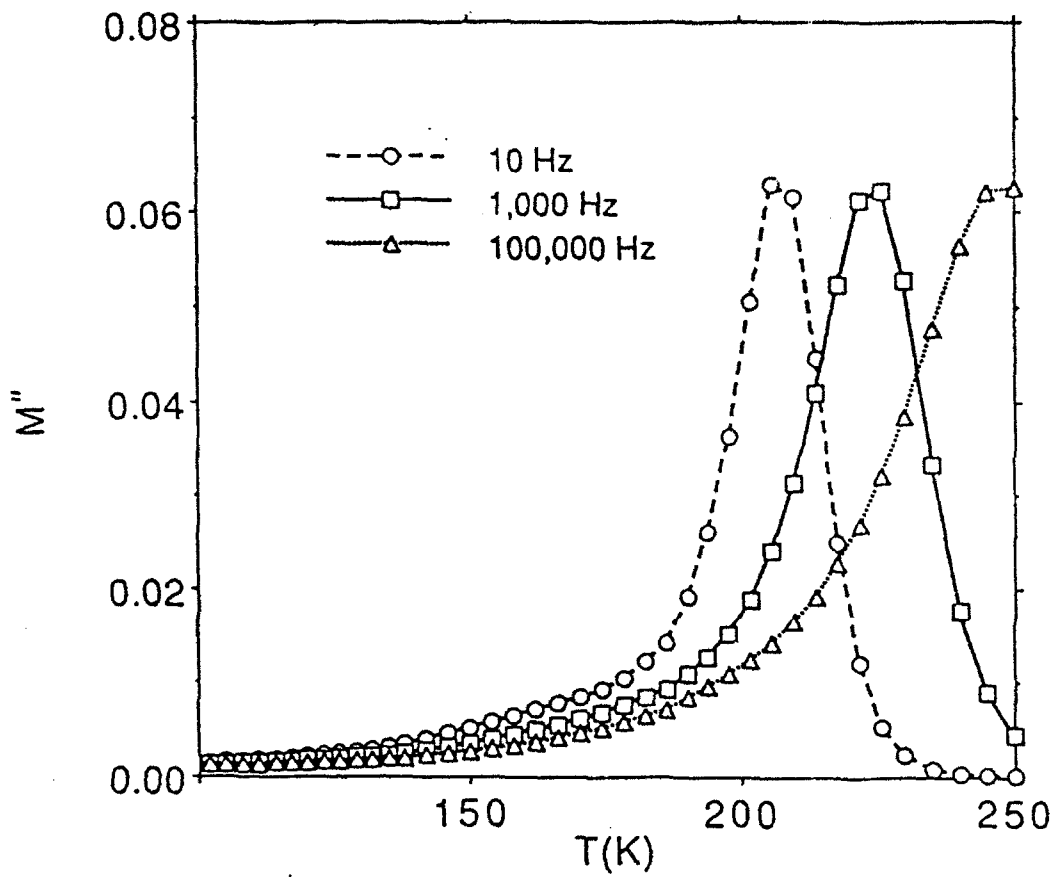


Fig. 12b
Chen et al.