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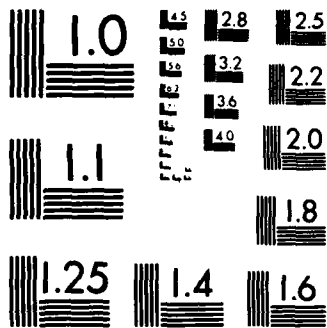
NMR, DSC, TMA, and High Pressure Electrical Conductivity Studies in

Solid, Crosslinked Dimethylsiloxane-ethylene oxide Copolymer Networks

Containing Sodium

by

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Audio frequency electrical conductivity and ^{23}Na NMR studies have been carried out on solid, crosslinked dimethylsiloxane-ethylene oxide copolymer networks containing sodium. The electrical measurements have been carried out in vacuum over the temperature range 5-380K and at pressures up to 0.65 GPa over the temperature range 230-380K. The electrical conductivity exhibits VTF or WLF behavior. From a VTF analysis, Ea is found to be about 0.11 eV and T_0 is found to be about 45°C below the "central" glass transition temperature as determined by both DSC and TMA. Also, T_0 is found to increase about 50 K/GPa and E_a increases significantly with pressure. In addition, the high pressure studies show that the activation volume associated with the electrical conductivity decreases from 44 to 23 cm^3/mol over the temperature range

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19. ABSTRACT (cont'd)

262-323K. The ^{23}Na NMR measurements reveal the presence of both bound and mobile sodium species, the relative concentrations of which change by about a factor of 10 over the temperature range -100 to +100°C. Broadening of the bound ^{23}Na line above room temperature suggests the possible presence of ion pairs or higher aggregates in the complex. Keywords: Solid electrolytes; Polymer electrolyte

NMR, DSC, TMA, AND HIGH PRESSURE ELECTRICAL CONDUCTIVITY STUDIES IN SOLID,

CROSSLINKED DIMETHYLSILOXANE-ETHYLENE OXIDE COPOLYMER NETWORKS CONTAINING

SODIUM*

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ABSTRACT

Audio frequency electrical conductivity and ^{23}Na NMR studies have been carried out on solid, crosslinked dimethylsiloxane-ethylene oxide copolymer networks containing sodium. The electrical measurements have been carried out in vacuum over the temperature range 5-380K and at pressures up to 0.65 GPa over the temperature range 230-380K. The electrical conductivity exhibits VTF or WLF behavior. From a VTF analysis, E_a is found to be about 0.11 eV and T_o is found to be about 45°C below the "central" glass transition temperature as determined by both DSC and TMA. Also, T_o is found to increase about 50 K/GPa and E_a increases significantly with pressure. In addition, the high pressure studies show that the activation volume associated with the electrical conductivity decreases from 44 to 23 cm^3/mol over the temperature range 262-323K. The ^{23}Na NMR measurements reveal the presence of both bound and mobile sodium species, the relative concentrations of which change by about a factor of 10 over the temperature range -100 to +100°C. Broadening of the bound [23]Na line above room temperature suggests the possible presence of ion pairs or higher aggregates in the complex.

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INTRODUCTION

Poly(dimethylsiloxane-ethylene oxide) (PDMS-EO) copolymers complexed with alkali metal salts have been receiving attention as solid electrolytes.[1-5] The primary reason, of course, is that in general siloxanes have very low glass transition temperatures and this feature is known to enhance ionic conductivity. In a recent paper,[5] several of the authors have reported the synthesis of a highly crosslinked (PDMS-EO) network containing sodium. In addition, various studies, including differential scanning calorimetry (DSC), ^{23}Na nuclear magnetic resonance (NMR), and vacuum electrical conductivity were presented. It was shown that the room temperature electrical conductivity was relatively large and that the complex had the advantages of being highly amorphous and stable. Consequently, the material is of interest as a potential solid electrolyte.

In the present paper, results for a differently prepared material are reported. In addition, new types of measurements have been carried out including thermomechanical analysis (TMA) and high pressure electrical conductivity.

EXPERIMENTAL

Preparation of a crosslinked P(DMS-EO):NaCF$_3$COO complex has been described in detail elsewhere.[5] In the present study the composition was slightly altered by adding approximately 33% PDMS to the P(DMS-EO) copolymer while keeping the EO/Na ratio fixed at approximately 8:1. This did not appear to improve the conductivity significantly, although the modified material did exhibit better mechanical flexibility. In addition, differences were noted in some of the thermal properties and NMR linewidths as discussed later.

The ^{23}Na NMR measurements were performed at 81 MHz utilizing standard pulse techniques. Fourier transform spectra were recorded following accumulation of 1000 free induction decays (FID's). Linewidths and relative intensities of the two resolvable lineshape components were extracted from the FID's by selective saturation and subtraction as discussed below.

Audio frequency complex impedance/electrical relaxation measurements have been carried out using a fully automated spectrometer. The key element in the measurements is a CGA-82 microprocessor-controlled bridge operating at seventeen frequencies from $10-10^5$ Hz. Vacuum measurements were carried out in a Precision Cryogenics CT-14 dewar controlled by a Lake Shore Cryotronics DRC-82 temperature controller using a silicon diode sensor. The high pressure measurements were carried out in a pressure vessel using Fluorinert (3M Co.) FC-77 electronic liquid as the high pressure fluid. For the electrical measurements, gold electrodes were vacuum evaporated onto the surfaces of the material in either a three-terminal or two-terminal configuration. The samples were about 1 mm

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thick and the electrodes about 4 mm in diameter. DSC and TMA measurements were carried out using a computer-controlled DuPont 990 console coupled with a 910 DSC and 943 TMA.

RESULTS

Thermal Analysis

Typical penetration TMA results for PDMS-EO complexed with sodium trifluoroacetate are shown in Figure 1. The primary feature of interest in the present work is the transition occurring at about -55°C. Since the material begins to soften at that temperature, the event is attributed to the glass transition. Further evidence is shown in Figure 2 where the DSC data are plotted. A feature typical of a glass transition is observed beginning at about -67° and ending at about -47°C. The central glass transition temperature, -57°C, is about 5° lower than for the higher EO content siloxane polymer studied previously.[5] The center of the DSC glass transition occurs at approximately the same temperature as the low temperature TMA softening.

A second feature is observed in the DSC which was not observed previously.[5] Specifically, there is an event at about 0°C. A corresponding feature was not observed in the TMA studies. Heating the sample at about 130°C decreased the temperature of this feature to about -15°C. Because of the variability of the temperature of this feature, it is not attributable to water. It is, in fact, similar to the DSC scans of Fish et al.[3] for a non-crosslinked ion containing siloxane polymer and thus the event may somehow be associated with the absence of crosslinking in regions of the material.

Electrical Conductivity

A typical low temperature complex impedance plot is shown in Figure 3. The data were analyzed using a Cole-Cole distribution:[6]

$$Z^* = \frac{Z_o}{1 + (i\omega\tau_o)^{(1-\alpha)}} \qquad (1)$$

where Z_o, τ_o, and α are the fitting parameters. As temperature increases, less of a semicircle is observed together with more slanted vertical line at lower frequencies representing blocking electrode effects. In most cases, a best-fit of equation (1) to the data was obtained allowing values for the bulk resistance of the materials to be determined. For the remaining plots, a combination of the depressed arc and slanted vertical line was used to determine the bulk resistance.

The conductance values, G, were then used, in conjunction with room temperature geometrical measurements, to calculate the electrical conductivity from:

$$\sigma = Gt/S \qquad (2)$$

where t is the thickness and S is the surface area. Thermal expansion effects are not included in the data analysis. The results of a typical vacuum data run are shown in Figure 4. The curvature often observed for amorphous polymer systems is apparent. Consequently, the conductivity data were first analyzed via the VTF equation:[7]

$$\sigma = AT^{-1/2} \exp^{-[E_a/k(T-T_o)]} \tag{3}$$

with the adjustable parameters A, E_a, and T_o. A non-linear least squares fit of equation (3) to the data was carried out and Table 1 contains the best-fit parameters.

It is noted that the vacuum values for T_o are about 40°C lower than the "central" T_g's which were determined by DSC or the softening temperature as determined by TMA. This result is consistent with all previous work by the authors.[5,8,9] Such results are not unexpected since $T_g - T_o$ is often on the order of 50°C for polymer systems.[10,11] Further, this phenomenon is consistent with the configurational entropy model[12,13] where T_o is interpreted as the temperature of zero configurational entropy which would be expected to occur at a much lower temperature than DSC T_g's. However, this result disagrees with those of other workers[12] for similar materials. Possible reasons for the discrepancy along with details of the data analysis technique used in the present work are given elsewhere.[5]

Next, isothermal data were taken and typical results are shown in Figure 5. The following equation:

$$\log_{10}\sigma = \log_{10}\sigma_o + aP + bP^2 \tag{4}$$

was best fit to the isothermal data and the best-fit parameters are listed in Table 2. The values listed in Table 2 for $\log_{10}\sigma_o$ are those calculated from the vacuum data i.e. absolute conductivities were not determined for the pressure runs. Rather, relative changes were determined and the absolute value normalized to the more accurate vacuum data.

The isothermal studies can also be used to determine activation volumes directly via:

$$\Delta V^* = -kT \; d\ln\sigma/dP \qquad\qquad (5)$$

The zero pressure values, those calculated from the slope of the conductivity vs. pressure plot at P=0, are listed in Table 2. The magnitude of the activation volumes is consistent with results for other ion conducting polymers and it is clear that they decrease as temperature increases. Also, the curvature of the Log(σ) versus pressure plot, which is related to the parameter b listed in Table 2, is negative at the lowest temperatures, becoming less so as temperature increases. Both results are similar to results for PPO complexed with lithium salts reported previously when the same analysis techniques were used[8,9] but opposite from the case of a single frequency analysis of results on ion containing PEO presented earlier.[14]

Next, the isothermal pressure data were used to generate 0.1 and 0.2 ∠Pa conductivities. The results were best fit to equation (3) and the parameters are listed in Table 1. Both the data and best fit curves are plotted in Figure 4. It is found that T_o increases about 5 K/kbar. This is between the trends observed for $PPO_8LiCF_3SO_3$ which showed a shift of about 10 K/kbar and PPO_8LiClO_4 and PPO_8LiI for which the shift was very small. Since glass transitions usually shift several K/kbar, this result is consistent with the usual assertion that T_o is somehow associated with T_g. Obviously, the configurational entropy model provides such an interpretation.

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Further, it is found that E_a also increases with pressure. As pointed out previously,[9] this provides evidence against "liquid-like" conductivity in these materials.

Next, the data were analyzed in terms of the WLF equation:[11]

$$\log_{10} \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T-T_g)}{C_2+(T-T_g)} \tag{5}$$

The resultant parameters are listed in Table 3. The values of C_1 and/or C_2 are somewhat lower than the "universal" values of 17.4 and 51.6.

Finally, for completeness, the data were analyzed via the mathematically equivalent VTF equation in the form:

$$\sigma = A' \exp^{-[E_a'/(T-T_o')]} \tag{6}$$

The results are listed in Table 1. It is interesting that on the basis of the RMS deviation it is equation 3 which best fits the data.

Nuclear Magnetic Resonance

The ^{23}Na absorption was previously shown to consist of a relatively narrow line with a short (approximately 1 ms) spin-lattice relaxation time (T_1) superimposed on a long T_1 (approximately 1 s) second-order quadrupole broadened line.[5] The composite NMR lineshape for the original sample,[5] hereafter denoted as sample A, is shown in Figure 6a. The dotted portion represents the absorption spectrum corresponding to the narrow line, which is obtained by saturating the long T_1 component. The spectra were taken at -76°C, well below T_g, wih sequence delays of 10s and 40 ms for the

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unsaturated and saturated lines, respectively. Figure 6b displays both

unsaturated and partially saturated spectra (at $T=-100^{\circ}C$) for the present

lower EO-content complex, hereafter denoted as sample B. The primary

difference between the two samples appears to be the greater degree of

broadening in the broad component of A. In fact, the broad line of B

(Figure 6b) is not second order quadrupole broadened as determined by the

values of the $\pi/2$ pulse widths for each lineshape component. The

full-width at half-maximum (FWHM) of the narrow line of B remains

relatively constant at approximately 5 kHz until about T_g, then narrows to

a minimum of 1 kHz at about $-5^{\circ}C$. At higher temperature, the line

gradually broadens to about 1.7 kHz as a result of extremely rapid

spin-lattice relaxation. The FWHM of the broad line of B remains between 7

and 10 kHz over the temperature range -100 to $100^{\circ}C$. However, a transition

from first to second order quadrupole broadening occurs at about $25^{\circ}C$.

This is in contrast to the results for sample A in which the broad

component exhibits second order quadrupole effects over the entire

temperature range.[5]

A common feature of samples A and B is the presence of both the

broad and narrow lineshape components throughout the temperature range -100

to $100^{\circ}C$. As the difference between the T_1 values of the two components

was always at least a factor of 100,[5] the individual contributions of each

line to the composite lineshape and hence their relative intensities could

be determined easily. The ratio of narrow to broad line intensity as a

function of temperature (for sample B) is shown in Figure 7.

The short-T_1, narrow line has been previously identified with highly

mobile Na^+ ions.[5] Among the possible configurations giving rise to the

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long-T_1, broad line are sodium ions rigidly bonded to the host polymer chains, and isolated cation-anion pairs or clusters. The presence of ion pairs in conducting polymer complexes has been inferred from a variety of measurements including vibrational spectroscopy[10] and pulsed field gradient NMR.[15] Conductivity measurements as a function of salt concentration in low molecular weight polyethers suggest that neutral ion pairs and charged ion triplets are the predominant salt species at low salt concentration.[16]

The possibility that the ^{23}Na broad line might be associated with ion pairs or higher aggregates is given credence by known quadrupole coupling constants for Na$^+$-anion pairs in the gas phase.[17] Figure 7 may then be representative of a temperature dependent pair (or aggregate) dissociation process, although the presence of an alternative Na configuration for the broad line, such as bonded to the polymer chains, cannot be ruled out. It is interesting to note that, according to the data in Figure 7, the Na$^+$ ion concentration increases by only a factor of 10 from -100 to +100°C, while the conductivity exhibits roughly a five order of magnitude increase over the same range. Thus, it appears that large scale segmental motion of the polymer chains implied by the VTF behaviour of the conductivity plays a much greater role than "carrier generation" in the transport process. A similar conclusion has been drawn by Watanabe et al.[18] who inferred the presence of a weakly temperature dependent dissociation process from time-of-flight mobility measurements in Li-PPO complexes.

Although there is considerable uncertainty in the higher temperature data of Figure 7 (due to the low signal to noise ratio characteristic of the broad line above room temperature) it is clear that the Na$^+$ ion

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concentration (narrow line) does not continue to increase with increasing

temperature, at least not at the rate observed at lower temperatures.

There is presently no satisfactory explanation for this observation, nor

does the high temperature scatter of the data permit further speculation on

this point. The final comment concerns the previously mentioned transition

to second order quadrupole broadening above room temperature. For the NMR

frequency employed (81 MHz), second order broadening implies a quadrupole

coupling constant on the order of 1 MHz, which is comparable to that of a

Na^+-anion pair.[17] It can be shown[19] that the quadrupole coupling

associated with a sodium ion in contact with a neutral ion-pair i.e. an ion

triplet, is somewhat smaller than for a sodium ion in contact with an

anion, i.e. an ion pair. Thus, the presence of a significant number of

triplets which are converted to single ions and ion pairs above room

temperature could provide an explanation for the observed broadening.

Further evidence for or against this simple model will require more

accurate narrow/broad ratios as well as better estimates of quadrupole

coupling constants from the observed lineshapes.

SUMMARY

In summary, then, the following results have been obtained.

(a) Vacuum electrical conductivity measurements have been performed

and are analyzed in terms of VTF and WLF equations. The most important

result is that for the VTF equation T_o is found to be about $45°C$ below the

"central" T_g. This is consistent with the usual behavior of these

quantities and is predicted by the configurational entropy model. As

regards the WLF equation, the values of C_1 and/or C_2 are found to be

slightly lower than the "universal" values.

(b) High pressure electrical conductivity measurements have also been performed and a VTF analysis showns that T_o increases about 50 K/GPa and E_a increases significantly. In addition, the activation volume associated with the electrical conductivity decreases as temperature increases as expected.

(c) ^{23}Na NMR-determined mobile to bound sodium ratios exhibit a factor of 10 increase over the temperature range -100 to +100°C, in contrast with the 10^5 increase in the conductivity over the same range. Thus, carrier generation plays a relatively minor role in the transport mechanism.

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Table 1. Best fit VTF parameters.

	RMS Deviation	$\log_{10}A$ $(\Omega\text{-cm})^{-1}-\sqrt{K}$	E_a(eV)	T_o(K)	RMS Deviation	$\log_{10}A'$ $(\Omega\text{-cm})^{-1}$	E'_a(eV)	T'_o(K)
Vacuum	0.0120	−0.63	0.102	171.7	0.0130	−2.03	0.097	173.5
0.1 GPa	0.0051	−0.43	0.115	176.7	0.0052	−1.81	0.111	178.1
0.2 GPa	0.0102	−0.26	0.127	181.3	0.0104	−1.63	0.123	182.4

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Table 2. Best fit parameters in equation 4 and activation volumes for isothermal data.

Maximum pressure (GPa)	T(K)	RMS Deviation	$\log_{10}\sigma_o$ $(\Omega\text{-cm})^{-1}$	$a(GPa)^{-1}$	$b(GPa)^{-2}$	ΔV^* (cm^3/mol)
0.15	262.2	0.0031	−7.530	−8.77	−2.21	44.0
0.27	266.5	0.0034	−7.276	−8.19	−1.44	41.8
0.23	272.3	0.0045	−6.968	−7.51	−1.48	39.1
0.30	280.5	0.0078	−6.588	−6.54	−0.70	35.1
0.60	306.6	0.0190	−5.692	−4.44	−0.49	26.1
0.55	317.9	0.0098	−5.405	−3.91	−0.23	23.8
0.40	323.4	0.0073	−5.281	−3.75	+0.17	23.2

Table 3. DSC results and best fit WLF parameters.

	$T_g(K)$	C_1	$C_2(K)$	$\log_{10}\sigma(T_g)(\Omega\text{-cm})^{-1}$	RMS Deviation
Onset	206	15.0	32.5	−17.0	0.0130
Central	216	11.5	42.5	−13.5	0.0130
End	226	9.3	52.5	−11.3	0.0130

FIGURE CAPTIONS

Figure 1. TMA plot showing the glass transition at about -55°C. The data were taken at 5 K/min.

Figure 2. DSC plot showing the glass transition at about -55°C. The data were taken at 10 K/min.

Figure 3. Complex impedance plot at 254K. + shows the center of the depressed Cole-Cole arc and x represents the bulk resistance of the sample. The squares represent the datum points and the solid line is the best fit Cole-Cole equation (equation 1).

Figure 4. Arrhenius plot of the electrical conductivity data. From top to bottom the data are vacuum (triangles), 0.1 GPa (diamonds), and 0.2 GPa (stars). The solid lines are the best fit VTF equation (equation 3).

Figure 5. Typical data and best-fit quadratic (equation 4) for the pressure dependence of the electrical conductivity. The data are at 306.6 K.

Figure 6. ^{23}Na NMR absorption spectra for (a) sample A, and (b) sample B (lower EO-content than A). The dotted curves in (a) and (b) are spectra obtained with a short sequence delay, in which the broad components are completely saturated.

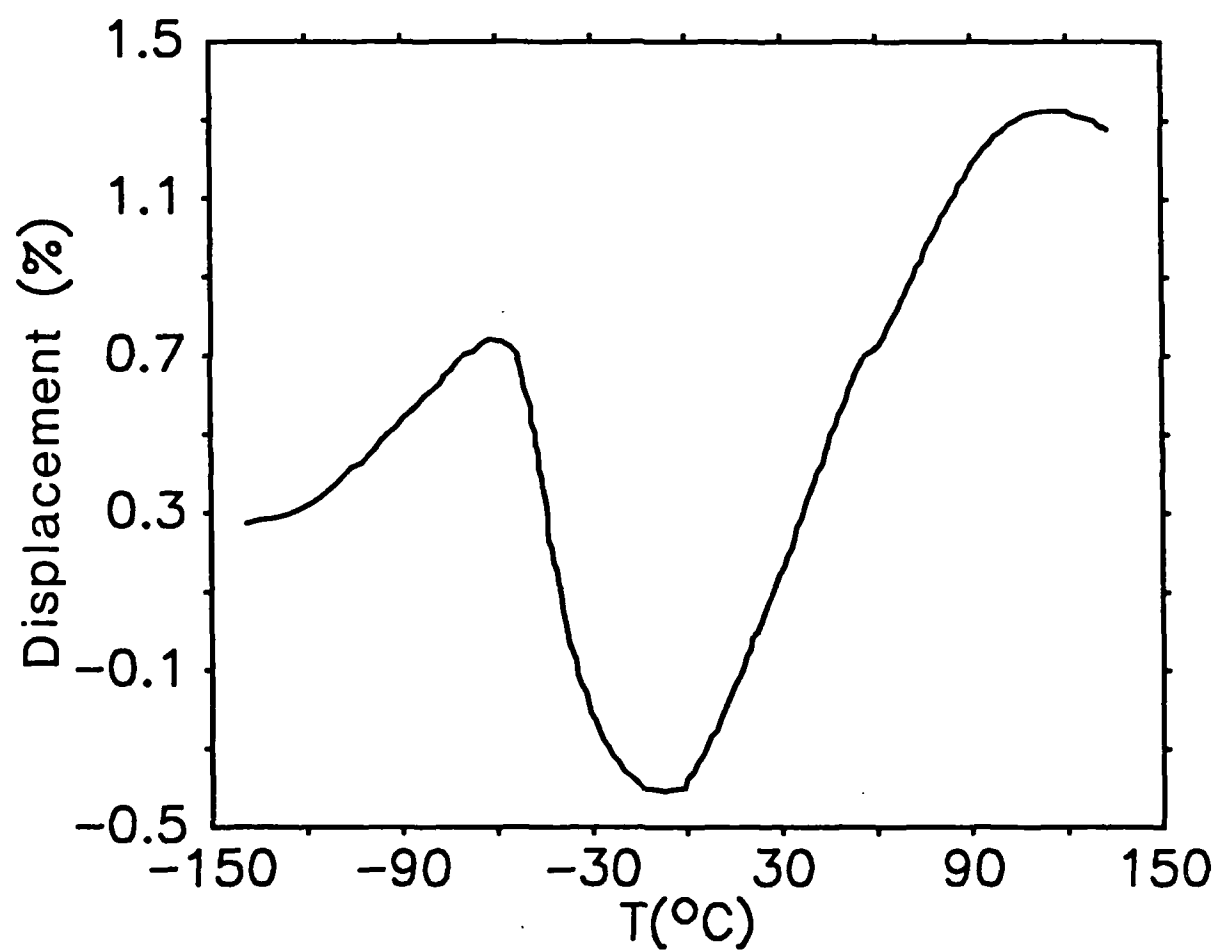Figure 7. Reciprocal temperature plot of narrow to broad line intensity ratios for sample B.
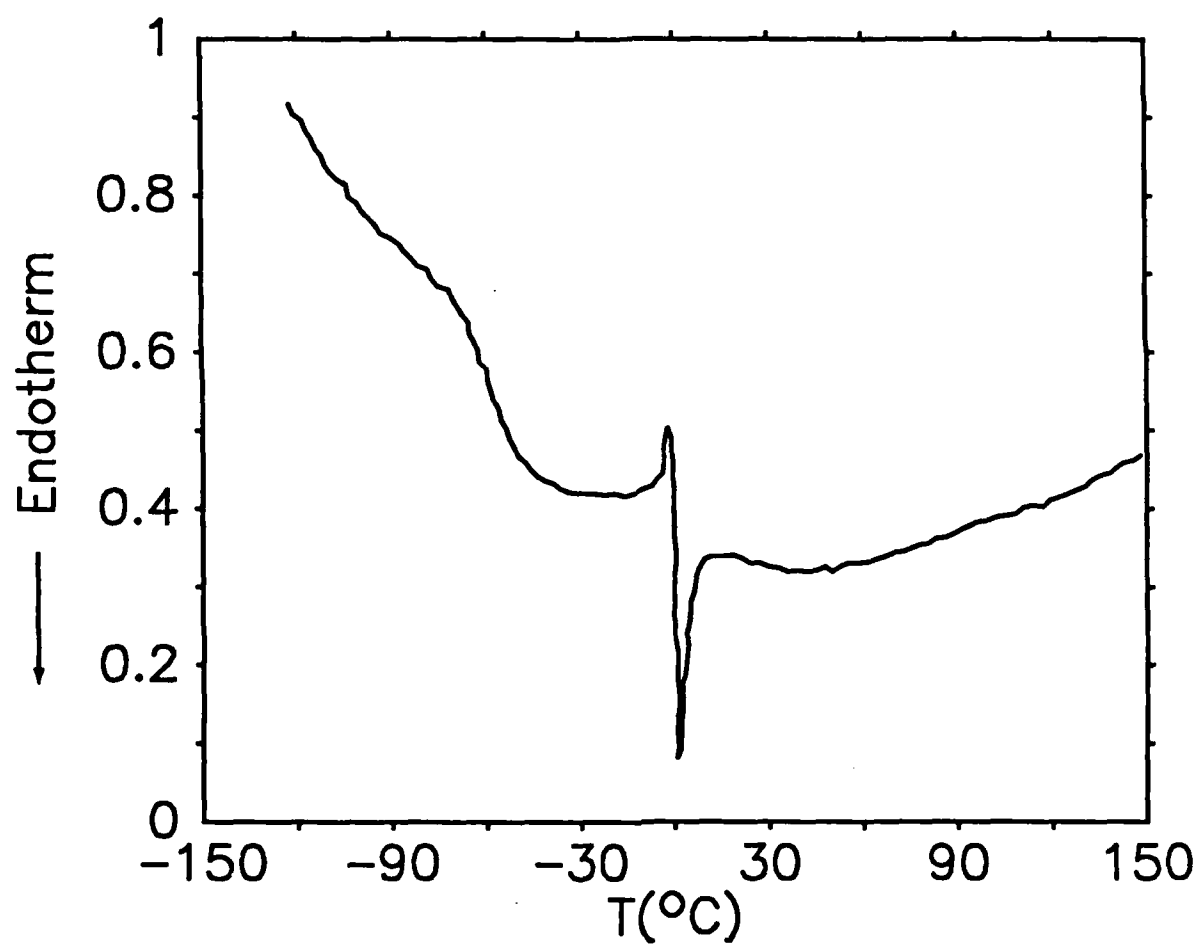
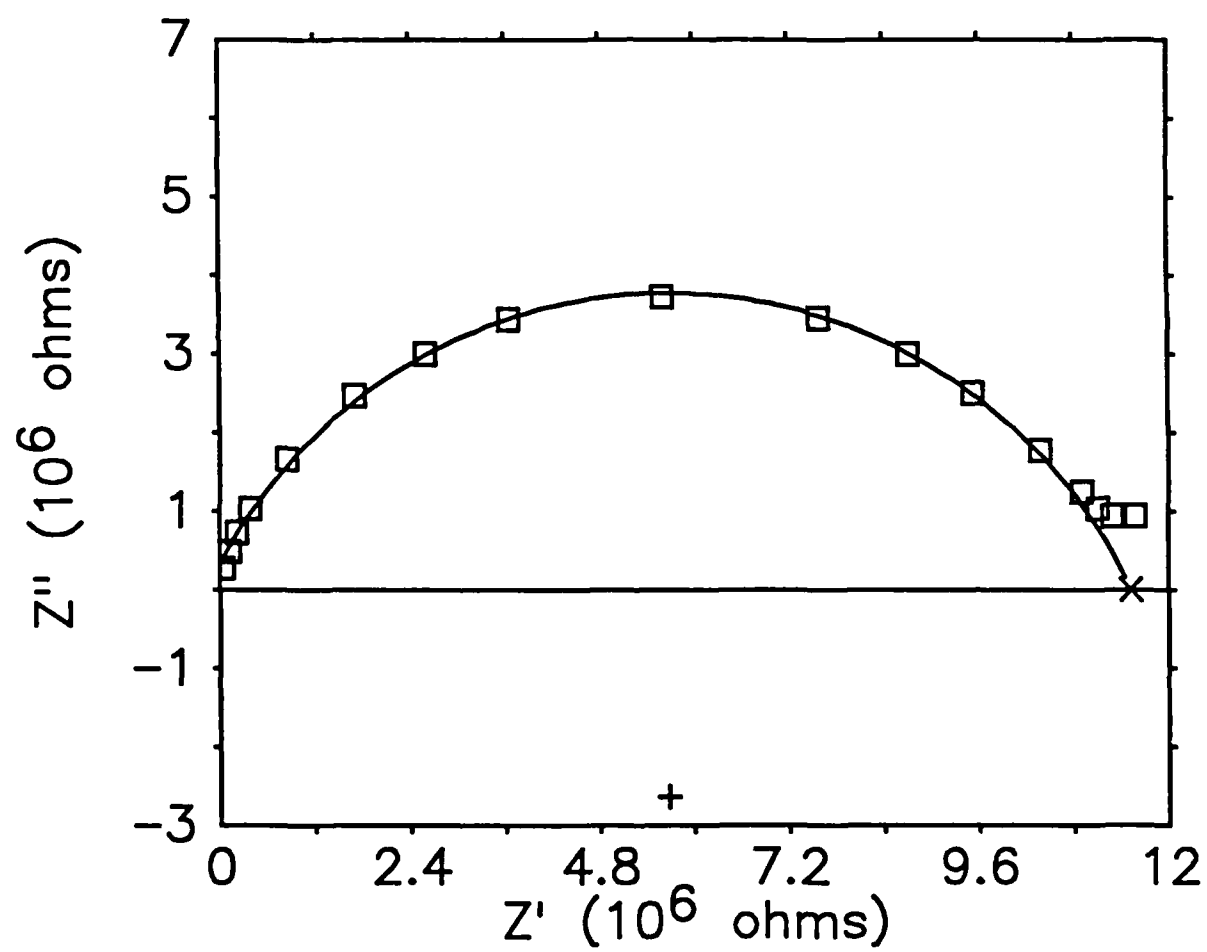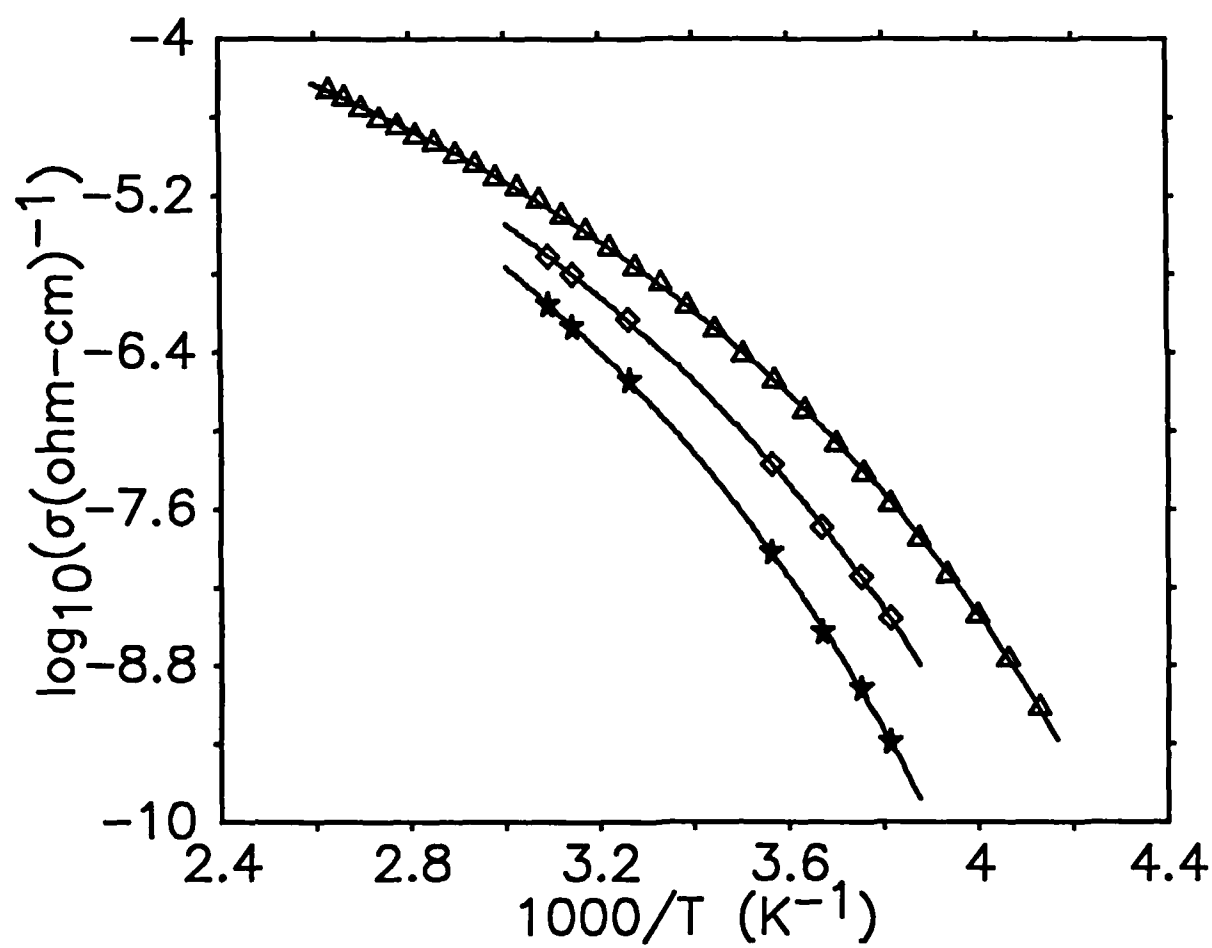Fig. 1 Wintersgill et al.

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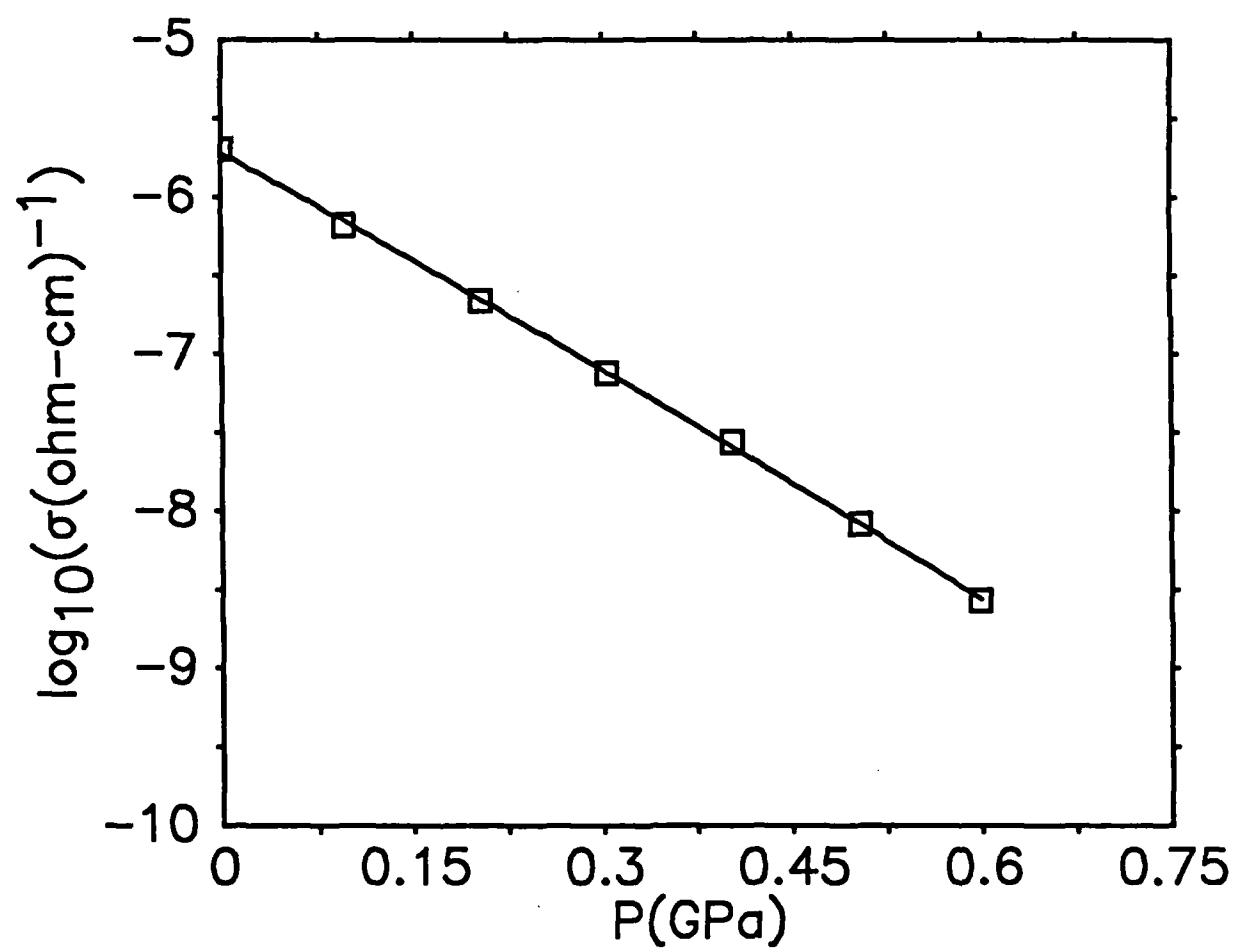
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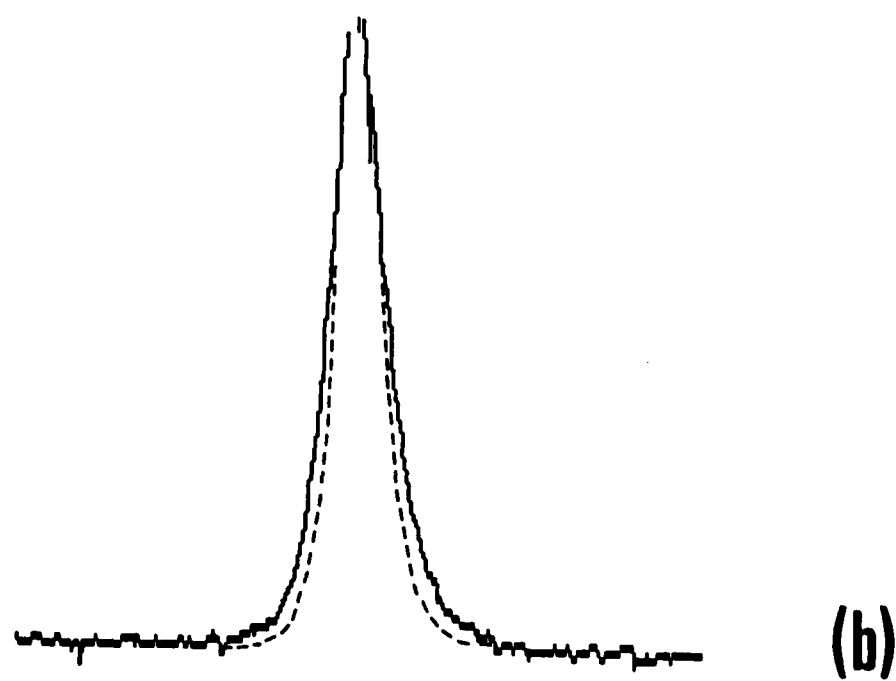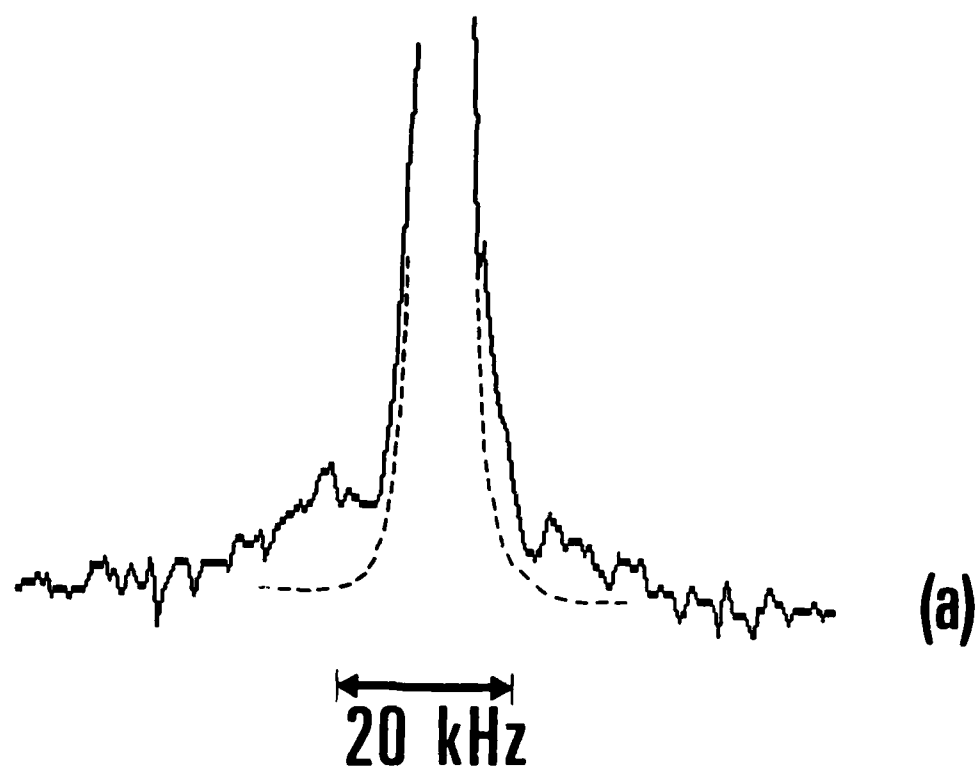Fig. 4 Wintergill et al.

Fig. 5 Wintersill et al.

20 kHz

(a)

(b)

Fig. 6

Fig. 7

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