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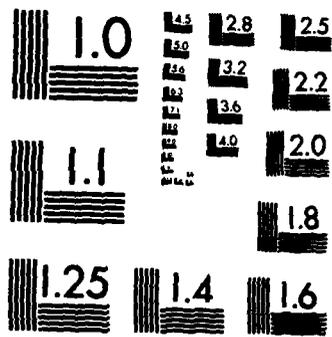
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NMP, ELECTRICAL RELAXATION, AND HIGH PRESSURE ELECTRICAL CONDUCTIVITY
IN ION CONDUCTING POLYMERS

by

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NMR, ELECTRICAL RELAXATION, AND HIGH PRESSURE ELECTRICAL CONDUCTIVITY IN ION CONDUCTING POLYMERS

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Recent nuclear magnetic resonance (NMR), electrical relaxation, and high pressure electrical conductivity studies of ion conducting polymers are reviewed. Most of the work discussed is that concerned with poly(ethylene oxide) (PEO) though some recent results concerning poly(vinyl acetate) are also described. A survey of experimental ^1H , ^7Li , ^{19}F , and ^{23}Na NMR data for ion conducting polymers based on PEO reveals some features that are commonly observed in superionic solids, such as motional narrowing in the temperature region of enhanced conductivity. The NMR activation energies are generally lower than those for conductivity, indicating the presence of localized motional processes. Previous electrical relaxation data along with new results for $\text{PEO}_4 \cdot 5\text{NaI}$ and $\text{PEO}_4 \cdot 5\text{LiCF}_3\text{SO}_3$ make it clear that PEO complexed with different salts exhibits different electrical relaxation spectra. Changes in chain structure are detected along with multiphase behavior. Also, new results are presented for the effect of high pressure on the electrical conductivity of poly(propylene oxide) complexed with alkali metal salts. Those results eliminate some ambiguities associated with previous high pressure electrical conductivity studies of PEO.

Introduction

Ion conducting polymers represent a class of materials of intense current interest. These materials are being considered for use as the electrolyte in solid state batteries. Battery development is, in fact, progressing rapidly.(1) Most of the work to date has centered on poly(ethylene oxide) (PEO). The first reports of fast ion conduction in PEO were due to Wright and co-workers.(2-4) Extensive work, however, began after the paper by Armand and co-workers.(5) Since then, there have been many studies of this polymeric solid electrolyte(6-39) along with reports of others such as poly(propylene oxide)(5), polyacrylonitrile,(40) poly(vinylidene fluoride),(40) poly(tetramethylene oxide),(41) poly(ethylene succinate),(42) and poly(vinyl acetate) (PVAc).(43)

Dielectric relaxation (DR) and nuclear magnetic resonance (NMR) techniques have been productively employed in studying fast ion processes in "traditional" solid electrolytes such as silicates, titanates, or aluminas which provide a framework for mobile monocations (e.g. Li^+ , Na^+ , K^+ , or Ag^+), or those of the heavy metal halide type (e.g. PbF_2 , ZrF_4) whose ionic conductivity is attributable to a partially disordered sublattice above some critical temperature. The primary reason is that both techniques are powerful tools for probing the local environment of ions. Another compelling reason for focussing on DR and NMR effects can be found in current theories concerning the apparent universality of low-frequency fluctuations, dissipation, and relaxation properties of condensed matter.(44) For example, fundamentally different measurements such as spin-lattice relaxation times and dielectric loss have shown remarkable similarity with respect to both temperature and frequency dependence for a wide variety of materials.(45) Consequently, both techniques have begun to be applied to ion-conducting polymers.

The study of DR in polymers has been going on for many years and there are several books on the topic.(46-48) Consequently, there already exists a considerable body of information on DR in "pure" PEO.(49-55) In fact, indications of fast ion conduction in PEO can be found in many of the early papers on "pure" PEO. For example, Ishida et al. attribute some of their observations to ionic conduction.(51) However, as is often the case, many questions about the origin of the relaxation phenomena remain. For example, it is easy to find at least four

different interpretations of the γ relaxation (47,55-60) not to mention three different nomenclatures (β (56), β_a (51), and γ (46,47)).

In the DR section of the present paper, recent results by one of the authors concerning DR in ion conducting PEO(37-39) will be reviewed and new results will be presented. Further, recent high pressure electrical conductivity studies in PEO(36) will be discussed along with some recent new results for poly(propylene oxide). There is not a great deal of published NMR work on ion conducting polymers at the present time. Some recent results will be discussed along with material drawn from earlier studies.

Discussion

Nuclear Magnetic Resonance

NMR studies of solid electrolytes have yielded important insights into both structural and dynamic properties, and several reviews of this rapidly growing field are in existence.(61-64) The power and versatility of the technique derive from the short-range nature of the nuclear quadrupole and dipole-dipole interactions. The quadrupole interaction occurs for nuclei with nuclear spin $I > 1$ (e.g. ^7Li , ^{23}Na) subject to an electric field gradient (efg) generated by a surrounding charge distribution of lower than tetrahedral symmetry. Quadrupole effects thus constitute a sensitive probe of local bonding arrangements. For nuclei with spin $I=1/2$ (e.g. ^1H , ^{13}C , ^{19}F) the nuclear dipole-dipole interaction is the predominant line-broadening mechanism since chemical shift effects usually provide a negligible contribution to broadening in the materials under consideration. The same argument applies to nuclei with $I>1/2$ situated in a highly symmetric charge distribution which yields a zero efg.

If atoms or ions can execute thermally activated motion, the dipolar fields experienced by their nuclei will be modulated with some characteristic "jump" frequency, ω_j . When ω_j exceeds the rigid dipolar linewidth ω_D , the nuclei sense a partially averaged dipolar field which gives rise to a phenomenon known as motional narrowing. Thus linewidth versus temperature measurements can yield important qualitative information about ionic or atomic motion. The nuclear spin-lattice relaxation time T_1 characterizes the nucleus' return to thermal equilibrium following a radio-frequency induced NMR transition, and as such, is also an effective probe of motional processes. The

Bloembergen, Purcell, and Pound (BPP) treatment of nuclear relaxation(65) predicts a T_1 minimum in the T_1 vs. temperature curve, corresponding to $\omega\tau=1$ where ω is the NMR frequency and $\omega_J\tau=1$. Another useful feature of T_1 measurements is that activation energies for ionic (or atomic) motion can be readily extracted from the data for simple Arrhenius behavior:

$$\omega_J = \omega_0 \exp(-EA/kT).$$

An important consideration in the context of solid electrolyte studies concerns the fact that T_1 is sensitive to local motion as well as long range transport processes and therefore does not always yield activation energies consistent with those determined by other techniques such as electrical conductivity.

High cationic mobilities in PEO-lithium salt complexes have been inferred from the observation of motional narrowing in ^7Li NMR spectra.(5,26) In $\text{PEO}_4:\text{LiCF}_3\text{COO}$ a single absorption line with no apparent quadrupole broadening is observed. The line begins to narrow at about 15°C and gradually decreases in width, becoming liquid-like at about 100°C .(26) Similar behavior has been noted in LiClO_4 -containing complexes.(32) An Arrhenius plot of the ^7Li linewidth temperature dependence is shown in Fig. 1 (data taken from ref. 32). The high temperature region of the curve yields an activation energy of about 11 kcal/mol which is somewhat lower than the conductivity activation energy of about 21 kcal/mol in the same temperature region. This discrepancy may be partly attributable to NMR's sensitivity to localized motion.

Proton NMR can shed light on the dynamics of the polyether chains just as ^7Li NMR can for Li^+ motion. The ^1H absorption spectrum of uncomplexed PEO at 35°C is shown in Fig. 2 ($f_0=400$ MHz). The most striking feature of the lineshape is its two-component nature, a narrow lorentzian superimposed on a broad gaussian. The broad component is identified with the relatively rigid CH_2 segments in the crystalline phase while the narrow line arises from flexible CH_2 segments in the elastomeric phase. ^1H spectra of complexed PEO also exhibit two-phase behavior, with a somewhat broader crystalline component linewidth than that observed in pure PEO (approximately 35°C). Fig. 3 demonstrates that motional narrowing also occurs for protons in $\text{PEO}_4:\text{LiCF}_3\text{COO}$ (data taken from ref. 24). The temperature of the onset of the narrowing appears to be the same for both phases

(approximately 30°C), with the elastomeric phase exhibiting a greater motional effect.

A plot of $1H$ vs. $1000/T$ is shown in Fig. 4. From the local minimum occurring at about 65°C, a motional correlation time of about 400 ps can be inferred. It should be noted that both the broad and narrow $1H$ components of $PEO_{4.5}:NaClO_4$ have approximately the same T_1 value, indicating the presence of an efficient spin-diffusion mechanism. (66)

Berthier et al. (27) have found that ^{19}F in $PEO_8:LiCF_3SO_3$ also exhibits an NMR spectrum consistent with the presence of both a crystalline and an elastomeric phase. The linewidths associated with each phase differ sufficiently to allow computation of their relative concentrations as a function of temperature. The temperature dependences of the fractions of protons and fluorines in the crystalline phase of $PEO_8:LiCF_3SO_3$ are shown in Fig. 5 (data taken from ref. 27). The discontinuity in the proton curve at 328 K is attributed to the melting of uncomplexed crystalline PEO. The absence of a similar feature in the fluorine curve indicates that the fraction of crystalline complex remaining above 328 K is salt-rich. It is of interest to note that certain PEO complexes such as $PEO_8:LiClO_4$ exhibit no crystallinity above the melting point of pure PEO. (27)

^{23}Na in $PEO_{4.5}:NaClO_4$ produces a single-component lineshape with no detectable quadrupole broadening, even at temperatures as low as -100°C. This finding is consistent with fourfold coordination of the Na^+ ion which has also been suggested by other investigations. (17) However, $PEO_{10}:NaI$ does yield a quadrupole broadened ^{23}Na spectrum (only the central $1/2, -1/2$ transition is observed at low temperature (27)) which suggests that variations in stoichiometry (and/or anion) will affect the average coordination of the cation.

Finally, poly(vinyl acetate) complexed with $LiClO_4$ also shows motionally narrowed 7Li NMR spectra. (43) Fig. 6 displays the temperature dependences of the full-width-at-half-maximum (FWHM) 7Li linewidth and 7Li T_1 . The similarity between PVAc- and PEO-based complexes (with respect to 7Li linewidths) suggests corresponding qualitative similarities of ion mobilities and perhaps transport mechanisms in the two different materials. The T_1 data points yield an activation energy of 0.11 ± 0.03 eV, about an order of magnitude less than the conductivity value which, again, is indicative of local motional processes sufficient for

nuclear relaxation.

Electrical Relaxation

DR studies provide an alternative, often complementary method of probing the motion of ions and their local environments, and has been applied to the study of polymers by many workers. In the experiments performed by the author, values of the conductance, G , and capacitance, C , were determined using a fully automated micro-processor controlled bridge constructed by CGA Associates, Cleveland, Ohio. The bridge operates at five audio frequencies over the range 100-10,000 Hz in equal logarithmic intervals and is interfaced with an Apple IIe computer. Some of the measurements are two terminal while others are three terminal using the parallel plate guard ring configuration.(67) Aluminum electrodes are evaporated onto the faces of the samples. The bridge is usually operated in the "conductance" mode where G/ω and C are read directly representing the equivalent parallel conductance and capacitance of the material. In general, the value of the real part of the dielectric constant, ϵ' , is determined at 300K and 1000 Hz using:

$$C = \epsilon_0 \epsilon' A/d \quad (1)$$

where A is the area of the plates and d is their separation. ϵ_0 is the permittivity of free space. In the absence of an experimental value for the linear thermal expansion coefficient, values of ϵ' at all other temperatures and frequencies are determined from:

$$\epsilon'_T = \epsilon'_{300} C_T/C_{300} \quad (2)$$

Values of ϵ'' are then calculated from:

$$\epsilon'' = \epsilon' G/C\omega \quad (3)$$

and in some cases this is transformed to a conductivity via:

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

One important feature of the measurement system is that eight samples can be placed in the same sample holder which allows careful inter-comparison of samples.

Typical results for ϵ'' vs. $T(K)$ at low temperatures for "pure" PEO are shown in Fig. 7. (37) Two relaxations are observed in agreement

with the literature. The first relaxation, α_a , has been unambiguously associated with the glass transition.(46,47) The identification of the second relaxation, γ , is not so clear from the literature. It has been variously attributed to a "crankshaft mechanism,"(57,58) "3-bond" or "4-bond" motions,(59,60) "chain end hydroxyl groups"(47) or the "tg+t \ddagger tg-t" transition.(55) In previous papers on dielectric relaxation in ion containing PEO(37-39) the data were interpreted in terms of the "tg+t \ddagger tg-t" transition. However, by preparing deuterated samples of PEO, the authors have recently obtained evidence that the γ relaxation in PEO is more likely to be due to hydroxyl groups at least some of which are probably at chain ends as suggested by Hedvig.(47) That data will be presented elsewhere. There is, however, one feature of the γ relaxation which is well documented. That is that the γ relaxation is essentially independent of the degree of crystallinity.(51) Consequently, in the discussion below concerning the γ relaxation, it is assumed that no distinction can be made between crystalline and amorphous phases of a given composition.

Figs. 8 and 9 show the relaxation spectrum for PEO_{4.5}:NaSCN and PEO_{4.5}:KSCN. The results for PEO_{4.5}:LiSCN are similar to those for PEO_{4.5}:NaSCN. There are no traces of α_a in any of the complexed materials. This shows that no amorphous pure PEO exists in any of the complexed materials. This is confirmed by differential scanning calorimetry studies.(68) In most cases, however, a thermal event is observed at about 60°C which is usually attributed to pure crystalline PEO. These materials, of course, are not fully complexed.

Next, as seen in Fig. 8, the γ relaxation for PEO_{4.5}:NaSCN is very similar to that for "pure" PEO. At first sight this would appear to be due to pure PEO. However, the materials are not very conductive(37) in agreement with the literature for highly complexed material. Further, the intensity of the peak is not diminished over that for "pure" PEO. Consequently, it was concluded(37) that the structure of the complexed polymer is not significantly different from that of "pure" PEO. The current interpretation of these results is that the sodium ions are smaller than the helical tunnel radius,(22) and this, combined with the linear configuration of the anion do not produce severe distortions in the polymer chains. More recent work by the authors show that there are, indeed, small differences

between the DR spectrum for PEO_{4.5}:NaSCN and that for "pure" PEO confirming that the peak is indeed attributable to complexed material and thus supporting the conclusions of the earlier report.(37) The new work will be presented in detail elsewhere.

However, as can be seen in Fig. 9, for PEO_{4.5}:KSCN, there is a drastic change in the γ relaxation region with at least three peaks being observed. Consequently, it was concluded(37) that the chains contain severe local distortions. This trend has recently been confirmed by the x-ray work of Hibma.(28)

A second example of large changes in the γ relaxation region is shown in Fig. 10 where some results for PEO_{4.5}:LiCF₃SO₃ are plotted. At least three relaxations are seen, none of which corresponds to the γ relaxation in "pure" PEO or to those observed in PEO_{4.5}:KSCN, for example. These results are interesting because there has been a great deal of work on this material. Careful studies of the variation of these relaxations with salt concentration are presently being carried out in an attempt to better understand the structure of these materials and hence gain insight into the origin of the various relaxations.

A final example of the type of relaxation phenomena observed in these materials is shown in Fig. 11 where ϵ'' vs. T(K) is plotted for PEO_{4.5}:NaI. The results are interesting as the temperature variation of the two relaxations is very similar to that observed for those in PEO_{4.5}:LiCF₃SO₃. Further work is necessary concerning this result.

As is apparent from the discussion thus far, the main thrust of the work to date has been to use DR to learn about materials. However, work has also begun toward using the materials to learn about DR. In particular, efforts are being made to evaluate the data in the light of various recent theories of DR.(44,45,69,70) An example of some preliminary results in this area are given in Fig. 12 via a "universal" plot of DR for the γ relaxation in "pure" PEO. That plot is constructed by best-fitting only five frequencies at a variety of temperatures. The best-fit curve is the theoretical form usually employed by Jonscher.(69,70) A new, fully-automated complex impedance measuring assembly operating at seventeen approximately equal logarithmic frequency intervals over the frequency range 10-100,000 Hz is currently operational and will make it easier to obtain plots such as Fig. 12.

High Pressure Electrical Conductivity

Of primary importance for these materials is the electrical conductivity. Typical high temperature conductivities are shown in Fig. 13. In order to gain information concerning electrical transport in these materials, the effect of high pressure on the electrical conductivity has been studied. The results for PEO(36) can be summarized as follows.

The magnitude of the variation of the electrical conductivity with pressure, and hence activation volume given by:

$$v \approx -kT(\partial \ln G / \partial P) \quad (5)$$

scale with the size of both the anion and cation. The simplest interpretation of this is that both the anions and cations are mobile. This agrees with several recent works concerning this material.(9,10,12,13,23) One of the ambiguities associated with these results, however, is that PEO is a multiphase system. For example, "pure" crystalline PEO forms easily and thus one must be concerned with the effects of pressure on the phase equilibrium. In order to eliminate this ambiguity, studies have recently been carried out on the effects of pressure on sodium salts in Parel (Hercules, Inc.), a highly elastomeric material consisting mostly of poly(propylene oxide) (PPO). The effects of pressures up to 0.3 GPa on the conductivity in this material are shown in Fig. 14.

It is clear that the activation volume is much larger for PPO8:NaClO₄ than for PPO8:NaSCN. This result is very similar to that observed in PEO8:NaClO₄ and PEO8:NaSCN and thus the likelihood that this effect is due to phase equilibrium of a pure crystalline phase with the conducting phase is eliminated. These results, do not, of course rule out the possibility that other phases may be affecting the data.

Finally, the order of magnitude of the pressure dependence of the conductivity in PPO-alkali metal salt complexes is very similar to that for PEO-alkali metal salt complexes.(36) Consequently, these results have the same implication concerning the transport mechanism in PPO as in PEO. Specifically, the fact that the conductivity decreases with pressure argues against a "chain transfer" transport mechanism.(71) The reason is that the effect of pressure is to decrease the spacing between the chains and thus should make jumps between chains

easier. Further, the magnitude of the decrease of conductivity with pressure is too large to be consistent with an intrahelical jumping process.(5) Specifically, the motion of the ions through the helical tunnels would not be expected to be greatly affected by pressure as the tunnels, themselves, should not be greatly affected. (Further evidence against this transport mechanism has recently been obtained by Dupon et al.(20)) This can be made quantitative via an approximate mode Gruneisen parameter defined by:

$$\gamma_a = -(\partial \ln \omega_a / \partial \ln V) \quad (6)$$

which can be calculated from:

$$v = 2\gamma_a g \chi \quad (7)$$

where g is the Gibb's energy and χ is the compressibility. Approximate values of χ and g yield $\gamma_a = 2$. This is much larger than mode gammas for intrachain vibrations(72) which would govern the intrahelical jumping process. Consequently, it was concluded that interchain fluctuations govern the transport mechanism and are the origin of an "interstice-interstice" jumping process.(36) In that paper, it was postulated that the ions move through the spaces between the polymer chains. In support of this is the fact that fast ion transport has now been observed in a wide variety of polymers as mentioned above and thus fast ion transport does not seem to require a specific chain structure. One final comment is that it appears that fast ion motion usually occurs only above the glass transition. Consequently, it appears that chain mobility also contributes to the conductivity.(5,17,22) This factor is consistent with the "interstice-interstice" jumping process in that it adds chain translation to chain vibration as a factor responsible for fast ion motion. Of course, there may be still other contributions to the decrease of conductivity with pressure and, in fact, "association" of the ions with the chains or with each other may contribute. The extent to which this factor is important has yet to be determined.

Summary

While the NMR results for several ion conducting polymeric systems reveal qualitatively similar features such as "classic" motional narrowing behavior common to superionic solids, there exist some important differences

between specific compositions. For example, changing the anion and/or the polymer/salt ratio has been observed to affect macroscopic properties such as the glass transition and microscopic structural arrangements such as the average cation coordination. Future T₁ studies for a greater variety of complexes are expected to lead to a better understanding of local hopping processes which, ultimately, may provide insight in conduction mechanisms. Electrical relaxation is well established as a very useful tool in studying ion conducting polymers. Changes in chain structure can be detected in addition to multiphase behavior. Finally, the effects of high pressure on the electrical conductivity provide useful information concerning the transport mechanism. The best picture at the present time is that in both PEO and PPO, both anions and cations move via an "interstice-interstice" jumping process. It is clear that more study is warranted, particularly with regard to systematic identification of compositional parameters which result in different kinds of structural or dynamic behavior.

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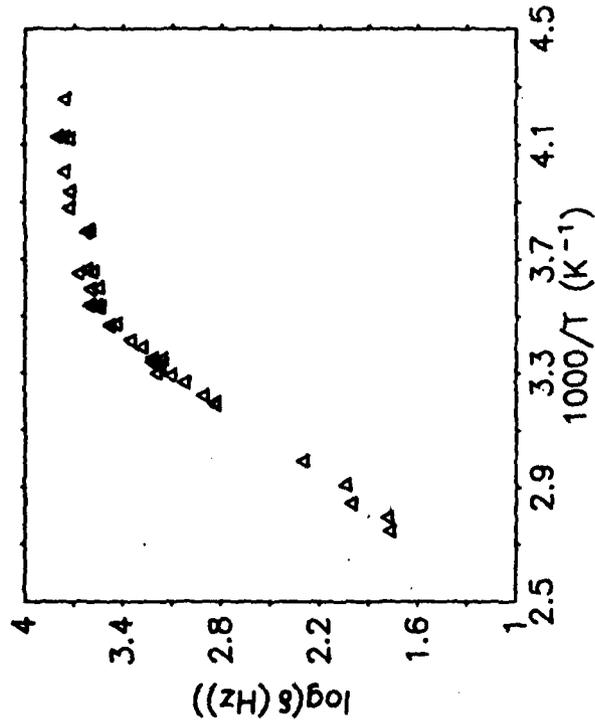


Fig. 1. Arrhenius plot of ${}^7\text{Li}$ linewidth (in Hz) in PEO-polyurethane-LiClO₄ network (from ref. 32).

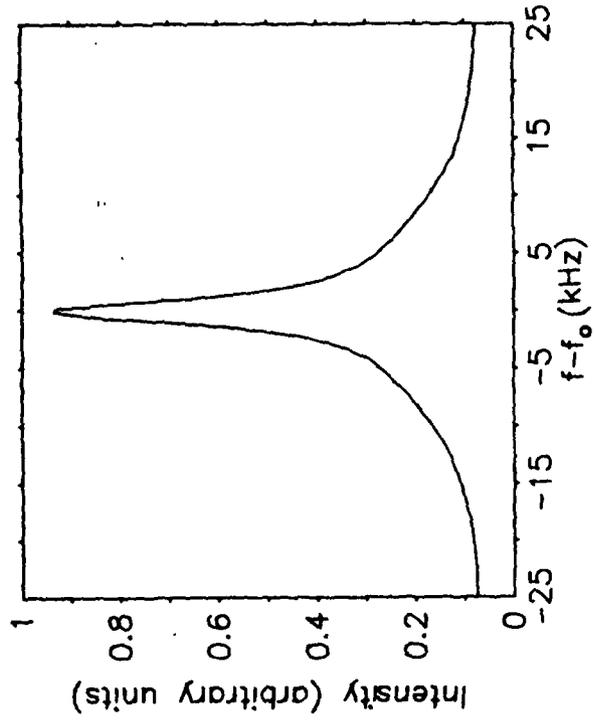


Fig. 2. Proton NMR lineshape of uncomplexed PEO (MW 5×10^6) at 35°C, $f_0 = 400$ MHz.

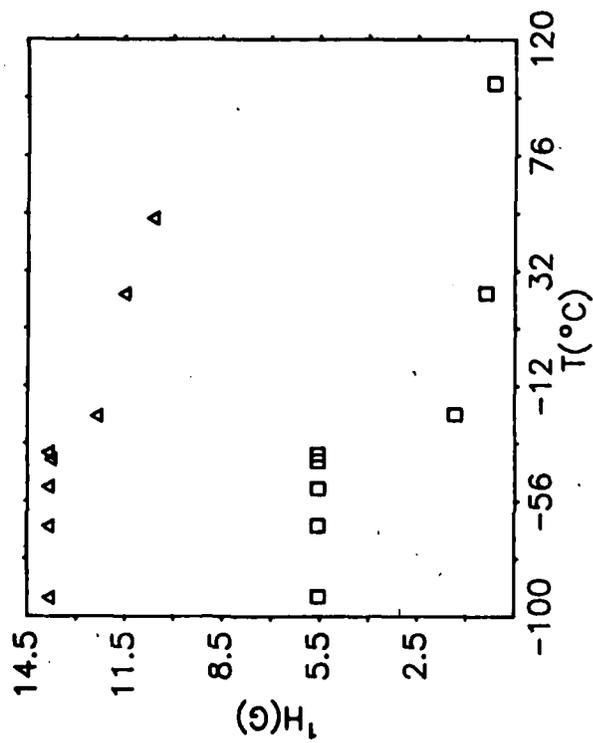


Fig. 3. Proton NMR linewidth (in gauss) vs. temperature in PEO₄:LiCF₃COO. Both components are shown (from ref. 26).

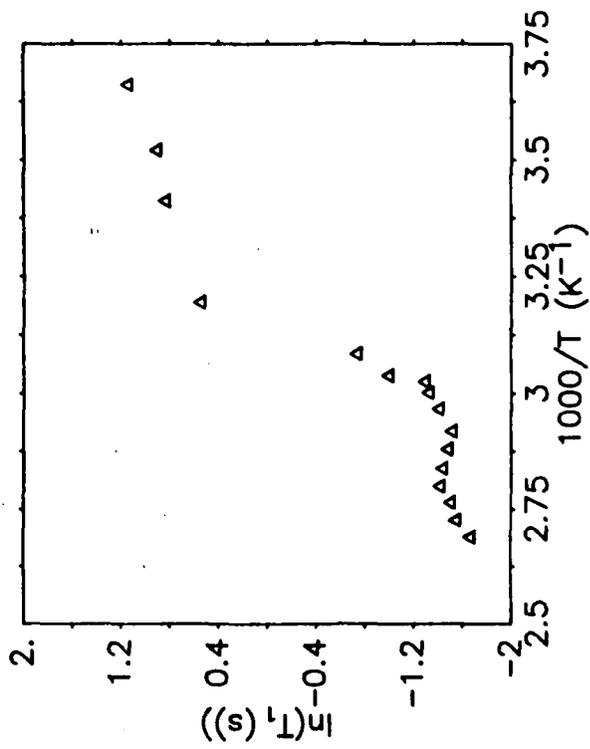


Fig. 4. ¹H T₁ vs. 1000/T in PEO_{4.5}:NaClO₄.

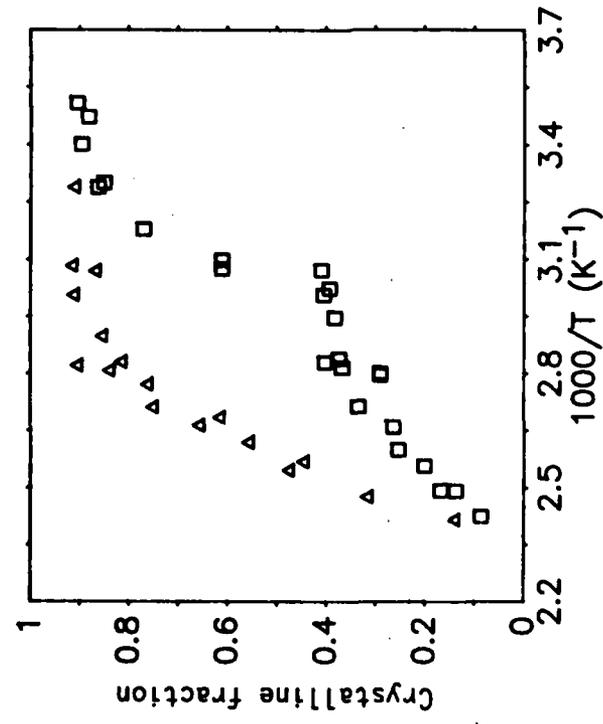


Fig. 5. Fractions of protons (squares) and fluorines (triangles) in the crystalline phase of PEO₈:LiCF₃SO₃ (from ref. 27).

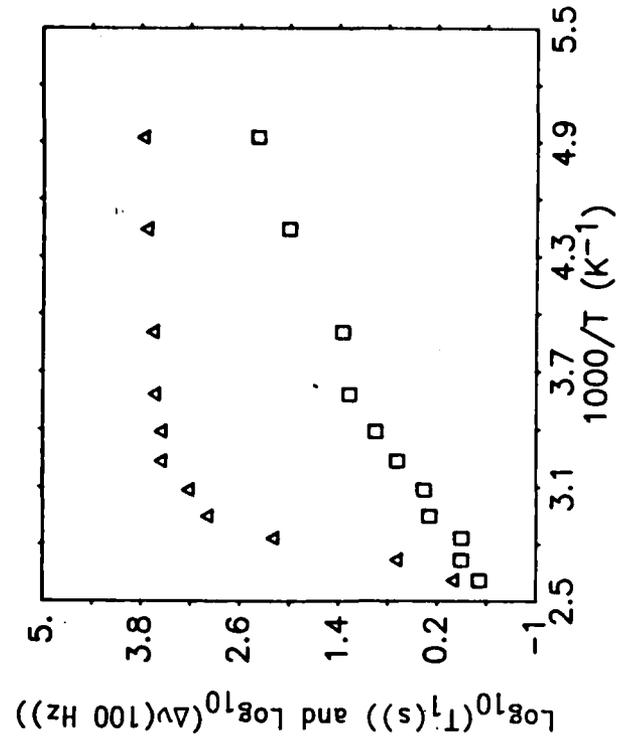


Fig. 6. Temperature dependences of ⁷Li linewidth (triangles) and T₁ (squares) in PVAc₈:LiClO₄ (from ref. 43).

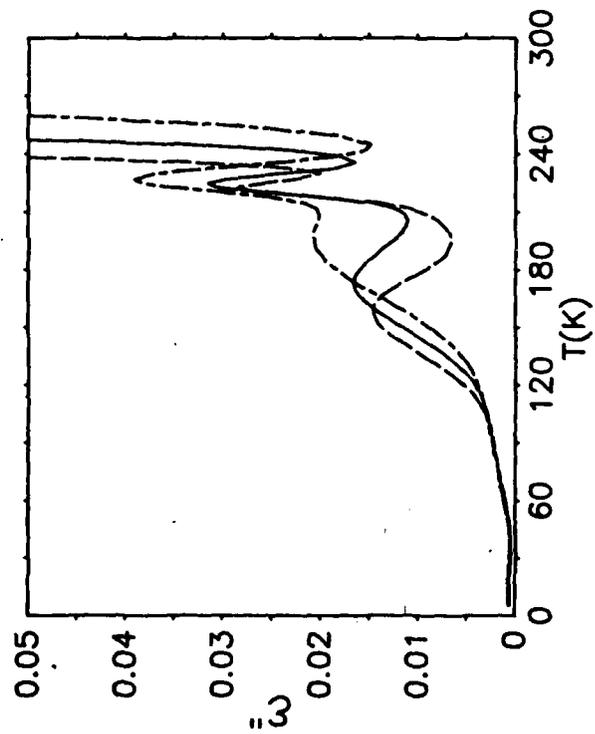


Fig. 7. ϵ'' vs. $T(K)$ for "pure" PEO (from ref. 37). The frequencies are: dash, 100 Hz; solid, 1,000 Hz; chain link, 10,000 Hz.

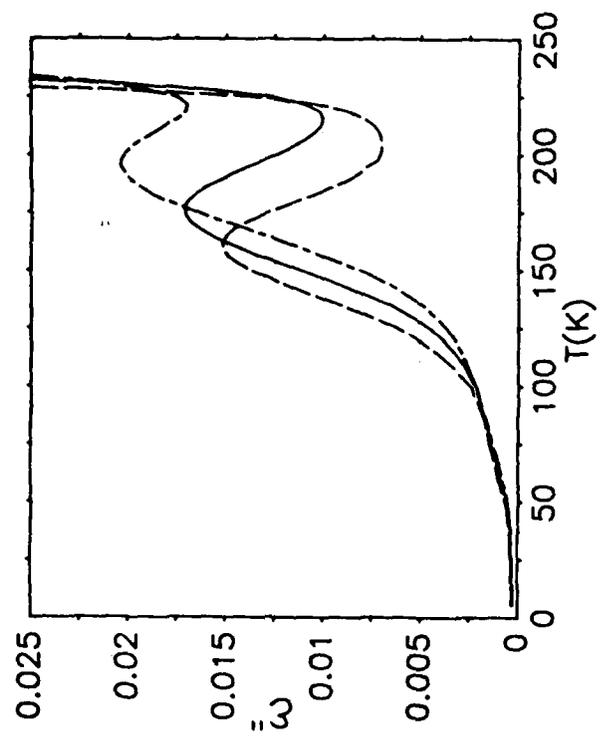


Fig. 8. ϵ'' vs. $T(K)$ for $PEO_{4.5}:NaSCN$ (from ref. 37). The frequencies are: dash, 100 Hz; solid, 1,000 Hz; chain link, 10,000 Hz.

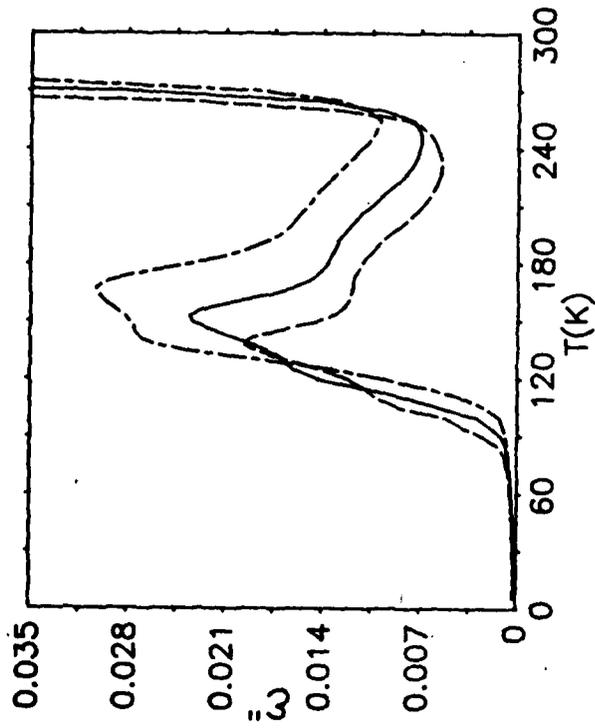


Fig. 9. ϵ'' vs. $T(K)$ for $PEO_{4.5}:KSCN$ (from ref. 37). The frequencies are: dash, 100 Hz; solid, 1,000 Hz; chain link, 10,000 Hz.

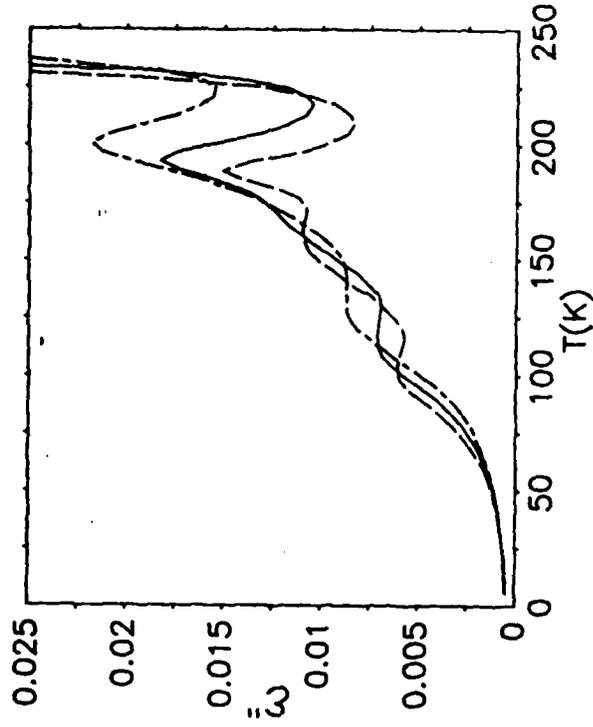


Fig. 10. ϵ'' vs. $T(K)$ for $PEO_{4.5}:LiCF_3SO_3$. The frequencies are: dash, 100 Hz; solid, 1,000 Hz; chain link, 10,000 Hz.

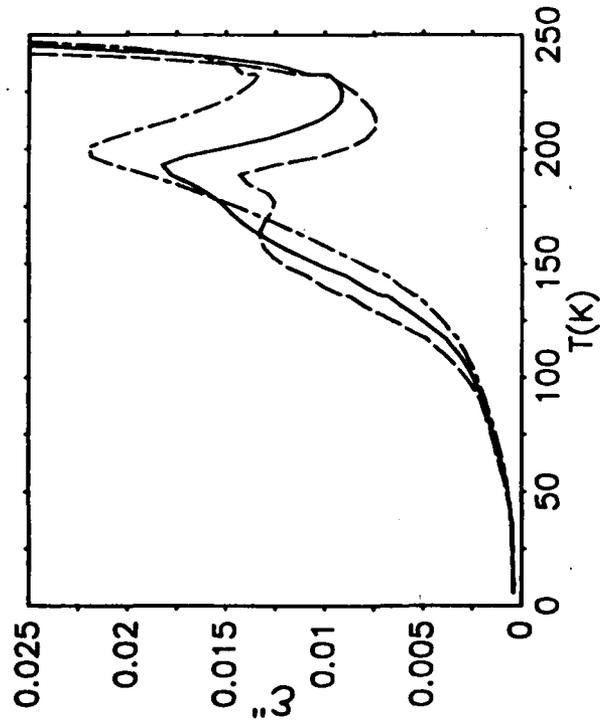


Fig. 11. ϵ'' vs. $T(K)$ for PE_{0.4.5}:NaI.
The frequencies are: dash, 100 Hz; solid, 1,000 Hz; chain link, 10,000 Hz.

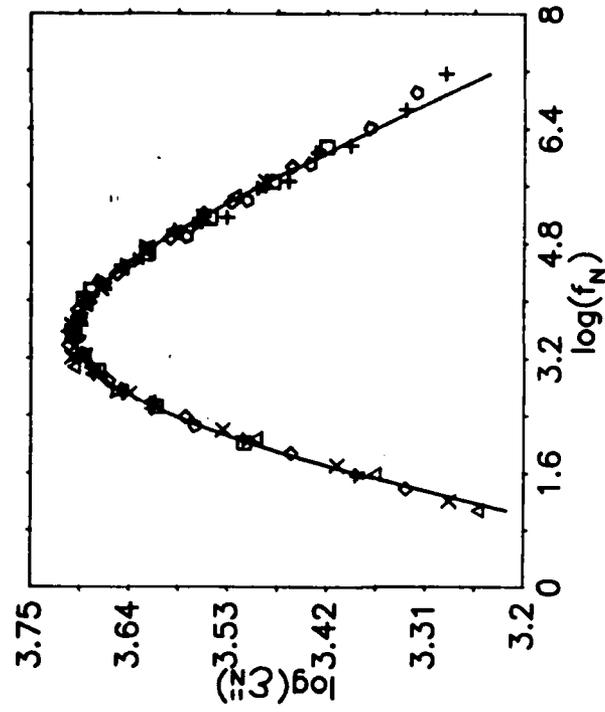


Fig. 12. "Universal" plot for the γ relaxation
"pure" PEO.

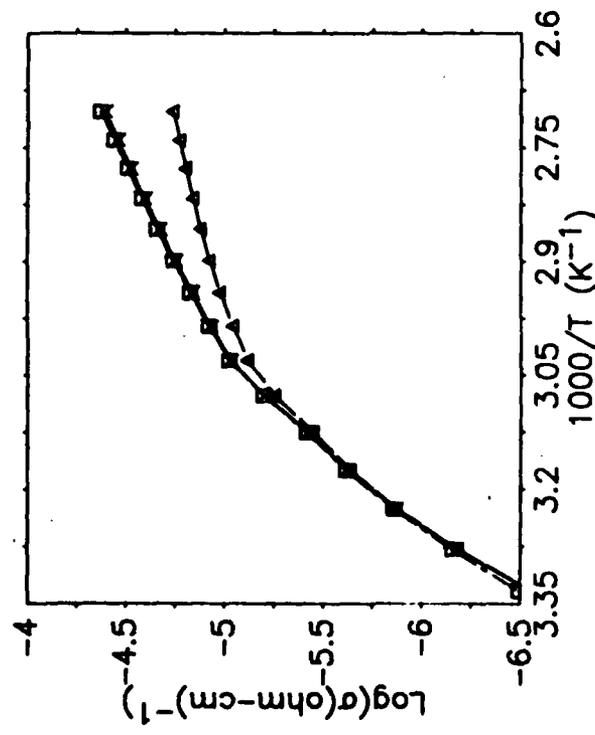


Fig. 13. $\text{Log}_{10}(\sigma(\text{ohm-cm})^{-1})$ for $\text{PEO}_{4.5}:\text{NaI}$. The frequencies are: triangles, 100 Hz; x, 1,000 Hz; squares, 10,000 Hz.

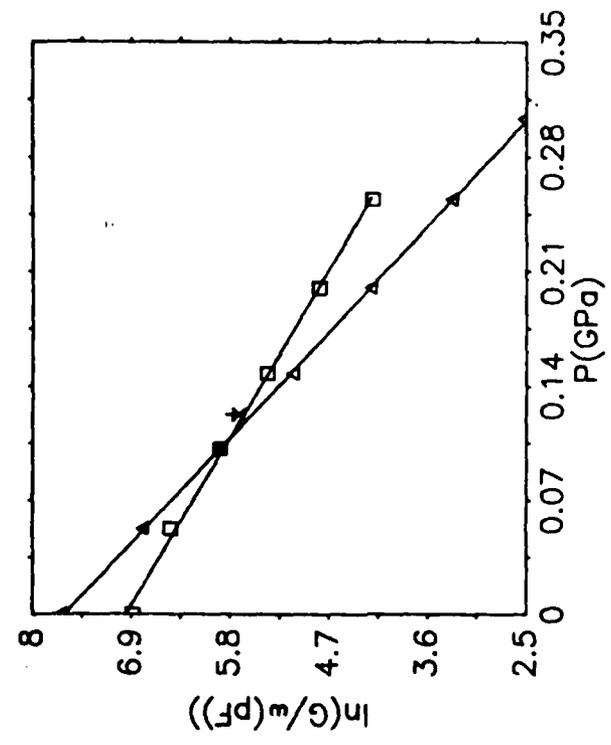


Fig. 14. $\text{Ln}(G/w(\text{pF}))$ vs. $P(\text{GPa})$ for $\text{PPO}_{8}:\text{NaSCN}$ (squares and plus) and $\text{PPO}_{8}:\text{NaClO}_{4}$ (triangles and x) at 86.90°C .

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