Thermal and dielectric properties of glassy ionenes*

F. Kremer, L. Dominguez, W. H. Meyer and G. Wegner†
Max Planck Institute for Polymer Research, D-6500 Mainz, FRG
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Poly[(dialkylimino)alkylene] salt ('ionenes')

$$-[-(CH_2)_m-N(R)_2-]_n\ q.n.X$$

where $m=6$ or 10, $R=-CH_3$ or $-CH_2CH_3$ and X = monovalent ($q=1$) or bivalent ($q=0.5$) counterions, form amorphous glassy films when quenched from the melt or cast from solution followed by rapid evaporation of the solvent. The glass transition temperature, T_g, was found to be between 295 and 350 K depending on the structure of the polymer and the type of counterion. The dielectric properties were studied in the frequency range 10–10^7 Hz and in the temperature range $-170<T<80°C$. The glassy polymers exhibit a dielectric relaxation at low temperatures assigned to a coupling of the motions of the methylene groups to the ionic centres in the polymer chain. The dielectric behaviour at high temperature is dominated by contributions of the ionic conductivity. At temperatures above a critical temperature T_{crit} (T_{crit} is 40–100 K below T_g) the conductivity increases strongly with increasing temperature and its frequency dependence becomes negligible. The temperature dependence of the conductivity follows an Arrhenius law with $1<E_a<1.5$ eV. The onset of this temperature-activated conduction process at T_{crit} coincides with the mechanical β-relaxation, the structural origin of which is still unclear. Extrapolation of the data yields values for the d.c. conductivity which are respectably high. Thus poly[(dimethylimino)decamethylene] tetrafluoroborate reaches a d.c. conductivity of 2×10^{-5} S cm^{-1} at 57.6°C.

(Keywords: thermal properties; dielectric; ionenes; polyelectrolytes; glass transition; ionic conductivity)

INTRODUCTION

The term 'ionene' is used as the trivial name for polymeric salts of which the poly[(dialkylimino)alkylene] salts

$$-[-(CH_2)_m-N(R)_2-]_n\ q.n.X \qquad (1)$$

are a simple example. In this paper we report on the dielectric properties and hence the ionic conductivity of some representative cases of this class of polymeric salts in their glassy state, where $m=6$ or 10 and $R=-CH_3$(Me) or $-C_2H_5$(Et); X is the counterion used to balance the positive charge of ammonium groups of the constituent units. Monovalent counterions such as tosylate (TOS), triflate (CF_3–SO_3), tetrafluoroborate (BF_4) and iodide (I) were used, for which $q=1$, for bivalent counterions such as tetrabromozincate ($ZnBr_4$), tetrabromocadmate ($CdBr_4$) and tetraiodomercurate (HgI_4), $q=0.5$.

In the following we will use the nomenclature I–*m*–R–X to describe the various combinations of the counterions with main chain and side chain elements; I stands for the general structure (1) and *m*, R and X are as defined in (1).

The dielectric properties of such ionenes, and hence their conductivity, have not been studied so far. However, some work has been reported on other polycationic systems with comparable properties. Chiang *et al.*[1] and Takahashi *et al.*[2] studied the conductivity of polyethyleneimine and quaternized polyethyleneimine, as well as their polymer–salt complexes. Conductivities of the order of 10^{-3} S cm^{-1} at 150°C were measured. Hardy *et al.*[3] reported conductivities of 1×10^{-5} and 6×10^{-6} S cm^{-1} for poly(diallyldimethylammonium)chloride and -triflate respectively at 26°C when plasticized with 58% polyethylenglycol.

D.c. conductivity measurements on these systems are limted by electrode polarization or blocking effects. Therefore, in this paper, the a.c. conductivity (10–10^7 Hz) was measured in the temperature range 100–400 K, to separate electrode polarization effects from the bulk conductivity. Furthermore, the results of the a.c. measurements allow for a detailed discussion of possible mechanisms of charge transport.

The ionenes I–10–Me–X and I–6–Et–X with X = triflate, tosylate and tetrafluoroborate do not recrystallize from the melt and form transparent films when cast from solution after fast evaporation of the solvent[4]. The same film-forming properties were shown by the I–10–Me–MY_4 with M = Zn, Cd, Hg and Y = Br, I, when cast from DMF or DMSO. The formation of glasses by fast cooling of the melt is convincingly proven by X-ray measurements. The X-ray powder diffractogram of I–10–Me–BF_4 shows sharp reflections of a well defined crystalline structure if slowly crystallized from solution. An amorphous halo is observed, however, if the same material is quenched to room temperature from the melt[4].

EXPERIMENTAL

The details of the syntheses of the ionenes and the preparation of the various salts by ion exchange have been described elsewhere[5]. The thermal properties were measured using a Mettler DSC-30 and a Perkin–Elmer DSC-7 analyser with a heating rate of 20 K min^{-1}.

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* Dedicated to Professor E. W. Fischer on the occasion of his 60th birthday

† To whom correspondence should be addressed

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For the dielectric measurements, polymer films were placed between two gold plated stainless steel electrodes that were pressed together by a micrometer screw. The polymer films with a thickness ranging between 20 and 50 μm were cast directly from solution on to one of the electrodes and the solvent was evaporated for 3 d in vacuum at 50°C. Care was taken to avoid contact with moisture and to work under water-free conditions. To provide good contact with the upper electrode of the sample condenser a gold counterelectrode was evaporated on to the polymer film using a mask with an inner diameter of 30 mm. The dielectric properties were measured in the frequency range 10–10^7 Hz using a Hewlett Packard Impedance Analyser (HP 4192 A). The measurements were performed in a purpose-built vacuum isolated cryostat. The temperature was varied between -170 and 80°C. The desired temperature was established using a temperature-controlled nitrogen gas jet. The stability of the temperature adjustment was ∓ 0.02°C over a period of 200 s, which corresponds roughly to the time needed for a logarithmic frequency sweep from 10 to 10^7 Hz with five steps per decade. The temperature of the sample was measured with a platinum resistor (Pt 100) inserted in the electrode on which the film was cast. The resistor was connected to a Keithly 195A Multimeter with a temperature resolution of ∓ 0.01°C.

RESULTS AND DISCUSSION

Thermal properties

Direct determination of the glass transition temperature, T_g, of ionenes with bromide (Br) as the counterion using differential scanning calorimetry (d.s.c.) was impossible due to the high crystallinity of these polymers. Attempts to determine it by plasticizing the samples with different polar solvents gave unsatisfactory results[6,7].

The fact that I–6–Et–X and I–10–Me–X with X = tosylate, triflate and tetrafluoroborate do not recrystallize after quenching from the melt allowed glass transition temperature of these polymers to be determined by d.s.c. The ionenes with divalent counterions, e.g. I–10–Me–X ($X = ZnBr_4$), do not recrystallize when cast from solution, while the ionenes with tosylate, triflate or tetrafluoroborate as counterions suffer from recrystallization after long times (one or two months at room temperature). *Table 1* shows the glass transition temperatures of the ionenes under study. They cover the range 295–350 K. The values of T_g were strongly influenced by the thermal history of the sample.

Tsutsui *et al.*[8–10] have studied the dynamic-mechanical properties of different aliphatic ionenes by torsional braid analysis[11]. The ionenes of the type I–*l*, *m*–Me–Br with $l = 6$, 12 and $m = 3$, 4, 5, 6, 8, 10 showed three relaxation regions: α, β, γ. The α relaxation was assigned to the micro-Brownian motion of the polymer segments in the amorphous regions and was correlated with the glass transition temperature. This relaxation was not observed for highly crystalline polymers, e.g. in I–6, 4–Me–Br and in I–6–Me–Br, and was strongly influenced by the preparation conditions of the sample. The ionenes studied by Tsutsui[12] exhibit glass transition temperatures in the range 345–406 K. Tsutsui *et al.*[9] reported that the glass transition temperature increases with increasing number of ionic centres per unit volume (ion density). Our d.s.c. measurements showed that the glass transition temperatures of the I–10–Me–X ionenes with X = I and BF_4 as counterions were 347 and 313 K, respectively. The fact that the glass transition temperatures reported by Tsutsui[12] for the I–6, 10–Me–X with X = I (377 K) and BF_4 (341 K) were higher than those measured for the corresponding I–10–Me–X can be explained by the lower ion density of the latter. The α relaxation was shifted to lower temperatures with increasing radius of the counterions for spherical counterions, while for non-spherical counterions this dependence was not straightforward. A clear dependence between the glass transition temperature and the dimensions or shape of the counterions could not be deduced from our d.s.c. results. However, the glass transition shifts to higher temperatures for ionenes with bulky divalent counterions than for ionenes with monovalent counterions (*Table 1*).

Table 1 Glass transition temperature of ionenes of general structure I–m–R–X as determined by d.s.c.

Polymer	$T_g \pm 3$ (K)
I–10–Me–TOS	315
I–10–Me–CF_3SO_3	295
I–10–Me–BF_4	313
I–10–Me–$ZnBr_4$	344
I–10–Me–I	347
I–10–Me–$CdBr_4$	350
I–10–Me–HgJ_4	338
I–10–Et–CF_3SO_3	313
I–10–Et–$ZnBr_4$	318
I–6–Et–TOS	312

The β relaxation as observed by Tsutsui appears in the region 223–273 K and was assumed to be due to the molecular motion of the ionic groups, but no detailed mechanism was suggested. It was noted that the intensity of this relaxation decreases with increasing crystallinity. The γ relaxation takes place around 143 K and was attributed to the local mode motion of the methylene groups. The γ relaxation was observed in crystalline as well as in amorphous ionenes and is common in polymers with methylene groups in their backbone, e.g. polyethylene, aliphatic polyamides and polyesters[10]. Tsutsui suggested that the γ relaxation has its origin in intrachain interactions that are transmitted along the polymer skeleton[9].

Dielectric properties

The dielectric data are characterized by the superposition of two processes: (1) a conductivity contribution that produces an increase of both the real part ε_1 and the imaginary part ε_2 of the dielectric function $\varepsilon^* = \varepsilon_1 + i\varepsilon_2$ with decreasing frequency; and (2) a relaxation process exhibiting a maximum in ε_2 that shifts to higher frequencies with increasing temperature (*Figure 1*). To separate these two processes the experimental data were fitted in their ε_2 dependence using the following equations:

$$\varepsilon_2(\omega) = \varepsilon_{2,\mathrm{cond}}(\omega) + \varepsilon_{2,\mathrm{relax}}(\omega) \qquad (1)$$

Attempts to fit the conductivity contribution to ε_2 with a single power-law term did not fit the measured dielectric loss within the limits of the experimental accuracy. However, it was possible to fit the conductivity contribution to ε_2 by the superposition of two exponential terms with strongly different temperature dependence, as follows:

$$\varepsilon_{2,\mathrm{cond}}(\omega) = A_1\omega^{N_1} + A_2\omega^{N_2} \qquad (2)$$

The factors A_1 and A_2 are strongly temperature dependent, in contrast to the exponents N_1 and N_2 (*Table 2*). The relaxation contribution was analysed quantitatively using the Havriliak–Negami equation[13]

$$\varepsilon_{2,\mathrm{relax}}(\omega) = \mathrm{Im}\left[\frac{(\varepsilon_1 - \varepsilon_n)}{(1 + (i\omega\tau)^{\alpha})^{\beta}}\right] \tag{3}$$

ε_l and ε_n describe the value of ε_1 at the low frequency and high frequency side of the relaxation respectively. α and β are constants that determine the width and asymmetry of the relaxation process. *Figure 2* shows the conductivity and the relaxation contributions to ε_2 as fitted using equation (1) for two different temperatures. It is noteworthy that the parameters α and β describing the relaxation process are nearly independent of temperature and of the type of counterion. An ionene which contained two monovalent counterions as a 1:1 mixture, namely I–10–Me–BF_4/PF_6 (1:1), exhibits the same dielectric behaviour as the ionene with only BF_4 as counterion, which is further evidence for the independence of the relaxation process from the type of counterion. Extrapolating the ε_2 maxima to low frequencies, one finds that at 1 Hz the relaxation takes place at ≈148 K. The dynamic-mechanical measurements performed by Tsutsui *et al.*[9,10] presented, in the same frequency and temperature range, a loss process due to the local mode motion of the methylene groups of the polymeric backbone, which was defined as γ relaxation. Such a local motion alone would not be dielectrically active because no change in the dipole moment is involved, but the fact that the movement of the methylene groups is transmitted to some extent to the polar ammonium group makes the γ relaxation dielectrically observable. The results of our dielectric measurements are also consistent with the observation of Tsutsui *et al.* that the γ relaxation in its breadth and location is nearly independent of the type of counterion.

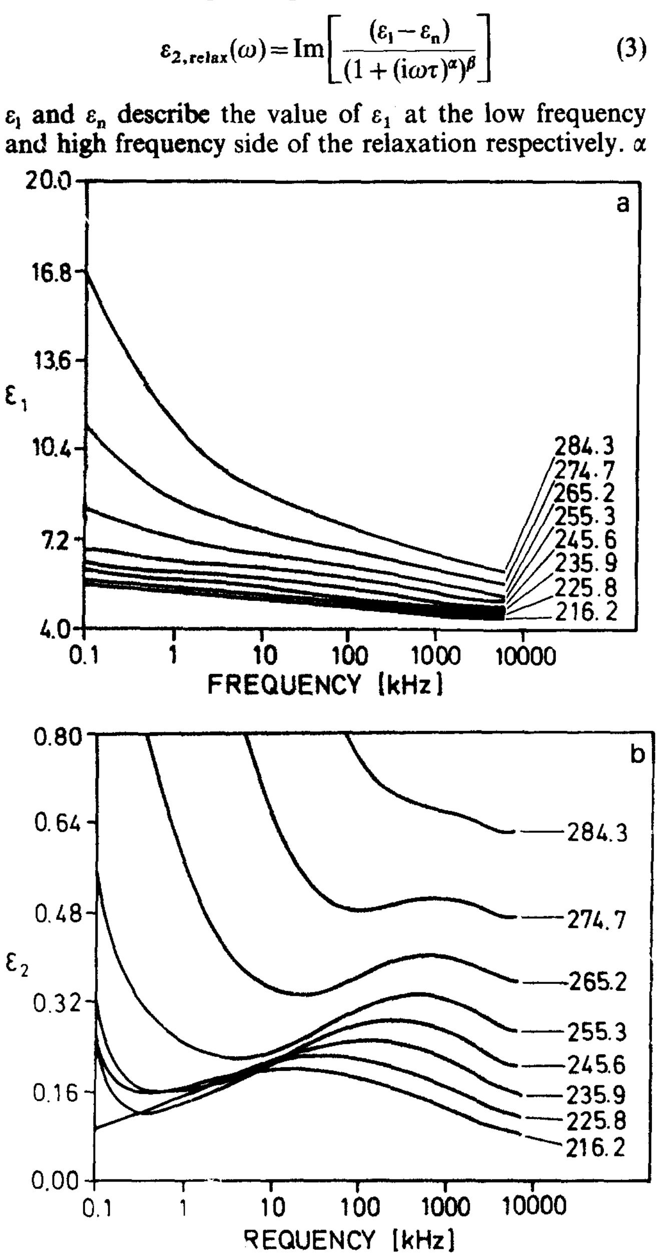

Figure 1 Frequency and temperature dependence of complex dielectric function for I–10–Me–Z : (a) real part (ε_1); (b) imaginary part (ε_2). Temperature is indicated on each curve (in K)

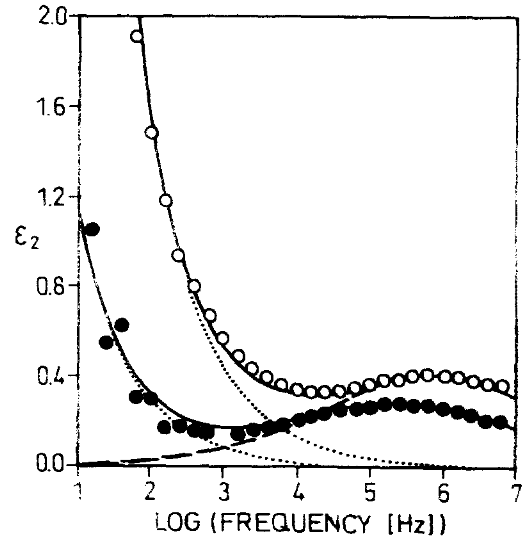

Figure 2 Fit of ε_2 according to equation (1) for I–10–Me–$ZnBr_4$: ●, 245.6; ○, 265.2 K. ·····, Conductivity contribution to ε_2; –––, relaxation contribution

Table 2 Fit parameters for conductivity and relaxation contribution to the dielectric loss ε_2 for I–10–Me–X ionenes with different counterions according to Equation (1)[a]

Counterion	Temp. (K)	$\Delta\varepsilon$	A_1	N_1	A_2	N_2	τ (s)
$ZnBr_4$	284.3	3.7	1.6×10^{-11}	0.5	1.0×10^{-9}	0.93	4.0×10^{-7}
	265.3	2.6	3.0×10^{-12}	0.5	9.0×10^{-12}	0.95	6.5×10^{-7}
	245.6	1.9	6.0×10^{-13}	0.5	1.0×10^{-12}	0.90	2.0×10^{-6}
	225.9	1.5	4.0×10^{-14}	0.5	2.5×10^{-12}	0.95	1.5×10^{-5}
	205.8	1.2	4.0×10^{-14}	0.5	2.5×10^{-12}	0.95	8.0×10^{-5}
BF_4	283.3	6.7	5.0×10^{-12}	0.4	8.0×10^{-9}	0.90	1.0×10^{-7}
	272.0	4.8	1.7×10^{-12}	0.4	1.3×10^{-10}	0.90	3.1×10^{-7}
	242.1	4.1	5.0×10^{-13}	0.4	2.0×10^{-12}	0.92	1.5×10^{-6}
	221.7	3.5	7.0×10^{-14}	0.4	1.0×10^{-12}	0.90	1.5×10^{-5}

[a] The values of α and β are not temperature dependent in the measured temperature range. For the sample with $ZnBr_4$ as counterion $\alpha=0.45$, $\beta=0.63$; for BF_4 as counterion $\alpha=0.46$, $\beta=0.63$

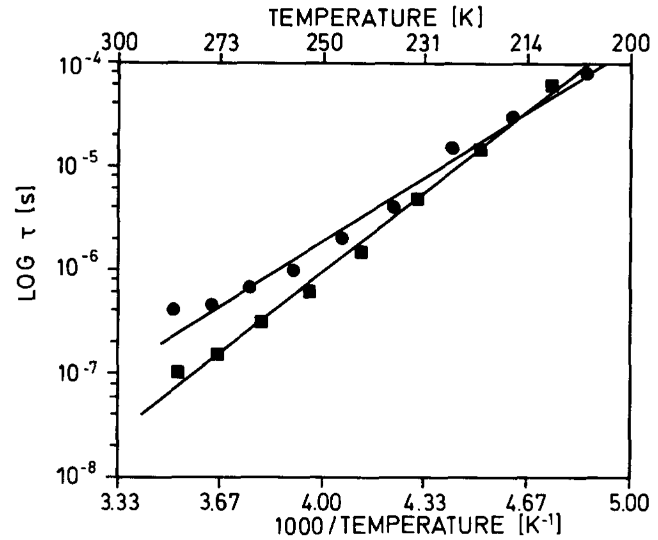

Figure 3 Temperature dependence of the mean relaxation rate τ (γ relaxation) for I–10–Me–X with different counterions; ■, $ZnBr_4$; ●, BF_4

The Havriliak–Negami fit of the relaxation process at different temperatures delivers the mean relaxation time τ, which exhibits an Arrhenius-like (*Figure 3*) behaviour. This is consistent with the temperature dependence shown by local mode motions in other polymeric systems[14]. The activation energy for the γ relaxation seems to depend to some extent on the type of counterion and was 0.35 eV for I–10–Me–BF_4 and 0.48 eV for I–10–Me–$ZnBr_4$. This may be explained by the difference in valence and size of these two counterions. Therefore, further studies on ionenes with other counterions are necessary to draw any conclusions on this particular topic.

The α and β relaxations observed by Tsutsui *et al.* in the dynamic-mechanical measurements were not found dielectrically. This is presumably caused by the strong contribution of conductivity processes at temperatures $>10°C$, which would cover the contribution of these relaxations. The logarithmic representation of ε_1 and ε_2 *versus* frequency shows how much stronger the conductivity contribution is, compared with the dielectric relaxation discussed above (*Figure 4*).

Since non-reactive electrodes were used, electrode polarization effects are to be expected. To analyse the extent of this effect, some of the data shown in *Figure 4* were plotted in the complex impedance ($Z = Z_1 + iZ_2$) representation (*Figure 5*). The real and imaginary parts of the complex impedance are defined as:

$$Z_1 = \frac{1}{\omega C_0}\left(\frac{\varepsilon_1}{\varepsilon_1^2 + \varepsilon_2^2}\right) \tag{4}$$

$$Z_2 = \frac{1}{\omega C_0}\left(\frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2}\right) \tag{5}$$

where C_0 is the capacitance of the empty condenser. Complex impedance arcs with depressed centres were found, with deviations towards the low frequency side. These deviations arise from electrode polarization[15] and become more pronounced with increasing temperature, and hence increasing mobility and increasing effective number density of the charge carriers. This proves that the assignment of the high frequency semicircles in *Figure 5* to a conductivity contribution is correct. From the complex impedance arcs at different temperatures it is possible to extrapolate the d.c. conductivity regarding the above mentioned electrode polarizations effects (*Figure 6*). The ionene I–10–Me–BF_4, for instance, has

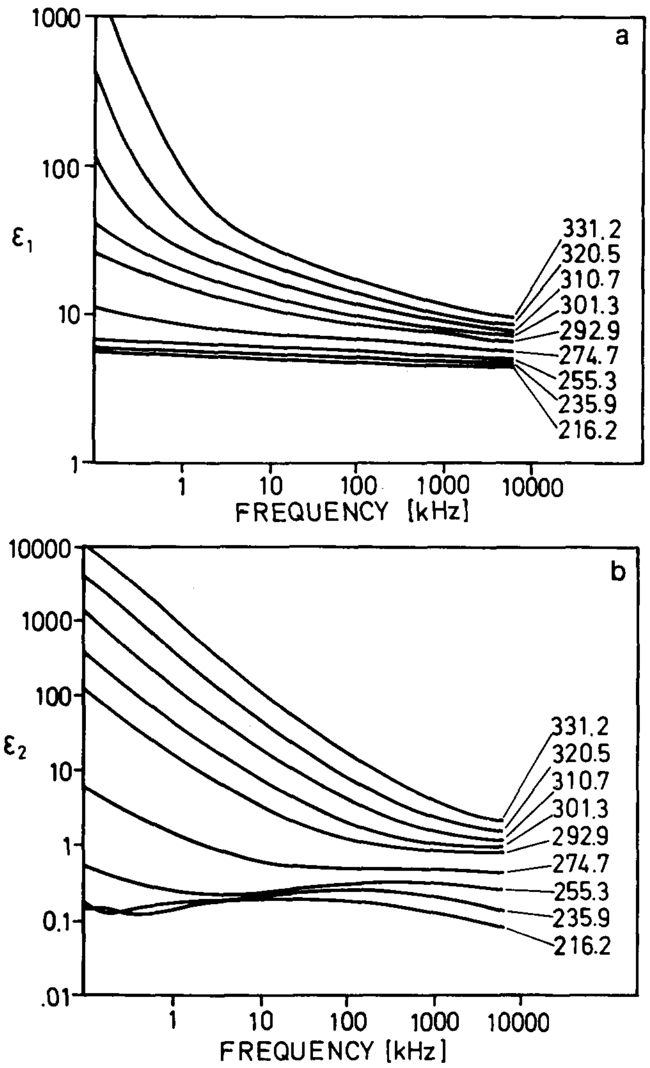

Figure 4 Frequency and temperature dependence of complex dielectric function for I–10–Me–$ZnBr_4$: (a) real part (ε_1); (b) imaginary part (ε_2)

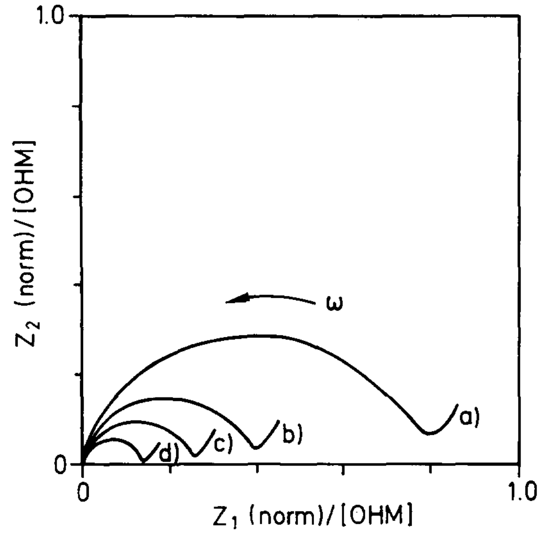

Figure 5 Complex impedance plots for some of the data presented in *Figure 4*: (a) 331; (b) 320; (3) 310; (d) 293 K

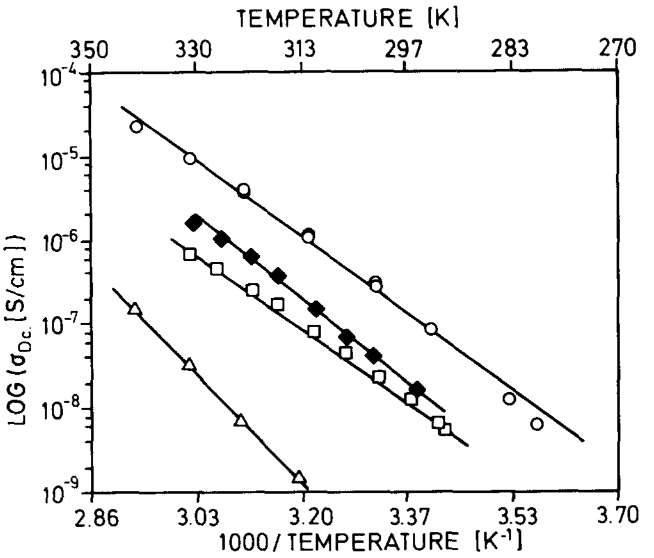

Figure 6 Temperature dependence of the extrapolated d.c. conductivity for ionenes with different counterions: ○, I-10-Me-ZnBr$_4$, $E_a = 1.03$ eV; ◆, I-10-Me-BF$_4$, $E_a = 1.01$ eV; □, I-10-Me-BF$_4$/PF$_6$(1:1), $E_a = 1.15$ eV; △, I-10-Me-ZnI$_4$, $E_a = 1.51$ eV

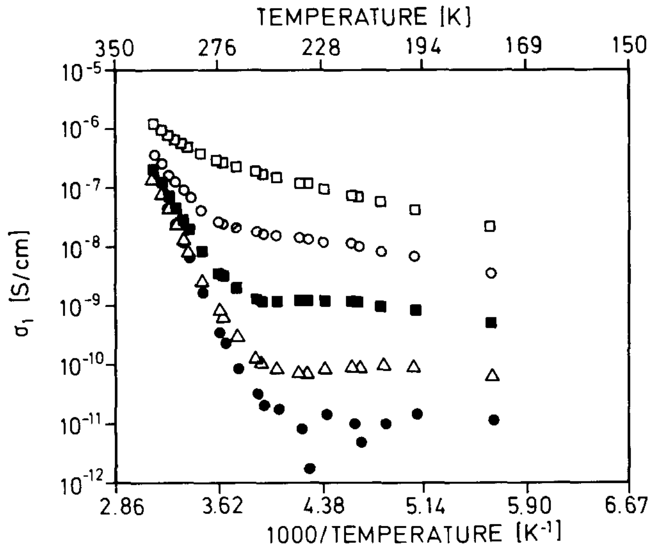

Figure 7 Real part of the complex conductivity for I-10-Me-ZnBr$_4$ *versus* inverse temperature (1000/T) for different frequencies (Hz): □, 10^6; ○, 10^5; ■, 10^4; △, 10^3; ●, 10^2

Table 3 Critical temperatures for the d.c. conductivity of I-10-Me-X ionenes with different counterions

Frequency (Hz)	T_{crit} (K)			
	ZnBr$_4$	ZnI$_4$	BF$_4$	BF$_4$/PF$_6$(1:1)
10^2	250	–	237	–
10^3	257	270	249	254
10^4	262	277	262	262
10^5	278	284	277	277
10^6	315	305	293	302

a conductivity of 2×10^{-5} S cm^{-1} at 57.6°C. These results are comparable to those reported by Hardy *et al.*[3] for poly(diallyldimethylammonium)chloride and -triflate respectively at 26°C, when plasticized with 58% polyethylenglycol.

The plot of the real part of the conductivity against the inverse temperature 1000/T (*Figure 7*) indicates that two conductivity regions are present. At low temperatures the thermal activation of the conductivity is almost negligible, but shows a strong dependence on frequency. After increasing the temperature above a critical value (T_{crit}) the conductivity increases strongly and the effect of the frequency on the conductivity becomes negligible at high temperatures. *Table 3* shows the influence of the frequency and the type of counterion on the transition temperature between the two conductivity regions.

For poly(ethyleneoxide) (PEO) or poly(propyleneoxide) (PPO) alkali salt complexes, an increase in conductivity is observed above the glass transition temperature of the polymer matrix[16]. The ionenes, in contrast, showed an increase in conductivity below their glass transition temperature (40–100 K below T_g). Another difference between the PEO alkali salt systems and the ionenes is that the temperature dependence of the conductivity of the former can be described by the Williams–Landel–Ferry or Vogel–Tamman–Fulcher equations[16], while the high temperature conductivity process (above T_{crit}) in ionenes follows an Arrhenius behaviour. At low temperature the conductivity is only negligibly temperature activated, but above the critical temperature activation energies for the d.c. conductivity between 1 and 1.5 eV are found (*Figure 7*).

The critical temperatures for I-10-Me-X with X = BF$_4$ and ZnBr$_4$ at 10 Hz were 253 and 243 K, respectively. On correlating these results with the dynamic-mechanical data reported by Tsutsui *et al.*[8–10], the critical temperature derived from our dielectric results obviously coincides with the temperature region at which the mechanical β relaxation takes place. This observation suggests that the β relaxation plays an important role in the charge transport.

The influence of recrystallization on the conductivity can be studied for the ionene I-10-Me-BF$_4$/PF$_6$ (1:1). This ionene forms glassy films when the solvent is rapidly evaporated, but recrystallization takes place on annealing at 60°C. As a consequence, the conductivity of this sample decreases dramatically when approaching this temperature. The same behaviour was observed for the ionenes with ether units in the main chain[4].

Figure 8 shows the complex conductivity $\sigma^* = i\varepsilon_0\omega\varepsilon^*$ (ε_0 is the vacuum permittivity) as a function of frequency at different temperatures for I-10-Me-ZnBr$_4$. The real part of the conductivity exhibits a behaviour typical of solid electrolytes[15,17]. The imaginary part of the conductivity (*Figure 8b*) shows the influence of electrode polarization at low frequencies.

The results from *Figure 8a* can be qualitatively summarized as follows:

(1) The conductivity increases with increasing frequency and temperature.

(2) For high temperatures, the conductivity is almost constant at low frequencies, but increases rapidly at a certain critical frequency.

(3) This critical frequency shifts to lower values with decreasing temperature.

(4) Above the critical frequency, the frequency dependence of the conductivity is proportional to ω^s with $0.5 \leqslant s \leqslant 1$.

The value of s increases with decreasing temperature (*Figure 9*). The same frequency and temperature dependence of σ^* is also found in other amorphous solids having a thermally activated hopping conduction[18–20].

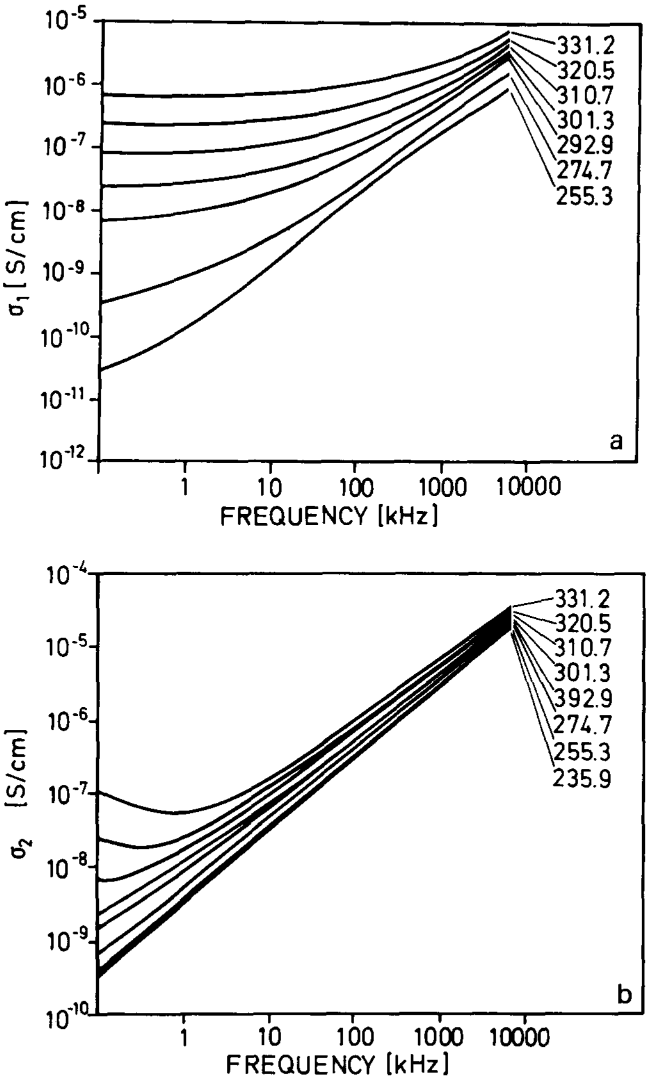

Figure 8 Temperature and frequency dependence of complex conductivity σ^*: (a) real part (σ_1); (b) imaginary part (σ_2)

To describe the frequency and temperature dependence of the complex conductivity a variety of mathematical approaches have been proposed[21–28]. However, the physical interpretation of these approaches is either non-existent or highly controversial[24,26]. A microscopic model was proposed by Funke[29–31]. He modified the Debye–Hückel–Onsager–Falkenhagen theory of conduction in electrolytes for solid ionic conductors. The basic concept is that the hopping motion of the mobile charged defects is largely determined by their mutual repulsive interaction. As a consequence, correlated forward/backward hopping processes take place which are responsible for the observed dispersion of the conductivity. The expression for the complex conductivity derived from these considerations is given by

$$\hat{\sigma} = \sigma_1(\infty) - \left[\frac{\sigma_1(\infty) - \sigma(0)}{1 + (\omega\bar{\tau})^s}\right] \qquad (6)$$

where $\bar{\tau}$ is the mean relaxation time between consecutive hops of a charge carrier from one site to another. The variation of the real part of the conductivity with frequency $\sigma_1(\omega)$ is found to be

$$[\sigma_1(\omega) - \sigma_1(0)] \approx \omega^s, \qquad \omega\bar{\tau} \ll 1 \qquad (7)$$

The experimental data obtained for ionenes as shown in *Figure 8a* are in qualitative agreement with this approach. A quantitative analysis using this additional information was not possible because the frequency range is too limited for the high frequency plateau described by Funke to be observed. Therefore, to determine the value of $\sigma_1(\infty)$ the conductivity needs to be measured at higher frequencies.

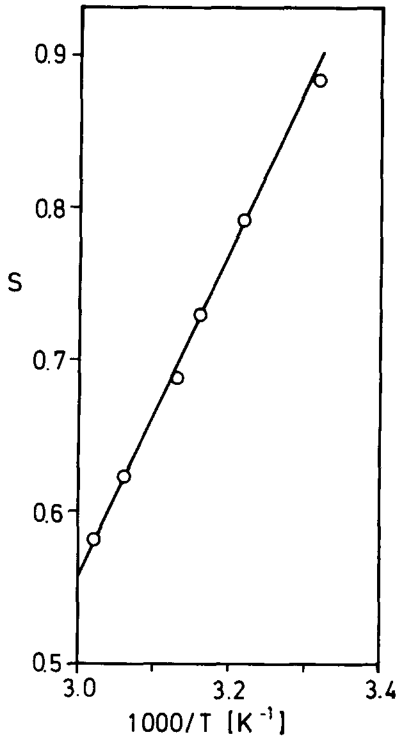

Figure 9 Parameter s of Equation (5) as a function of inverse temperature at 1 MHz for I–10–Me–ZnBr$_4$ (data from *Figure 8a*)

It is interesting that the experimental results are also in qualitative agreement with the concept of diffusion-limited relaxation and recombination in disordered solids as developed for amorphous semiconductors by Movaghar[32].

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