Dielectric properties of glassy cationic epoxide–amine addition polymers

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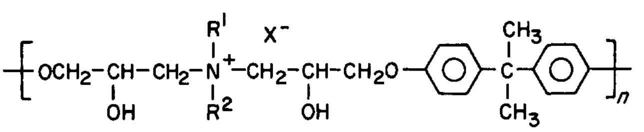
Glassy cationic polymers were synthesized by N-alkylation of linear high molecular weight epoxide–amine addition polymers:



$R^1 = CH_2C_6H_5, CH_2CH_2OH$
$R^2 = CH_2C_6H_5, CH_3, CH_2CH_2CH_2CH_3$
$X = Cl, Br, I$

The dielectric properties, measured over the frequency range of 10^2–10^7 Hz and at temperatures between 100 K and 400 K, are characterized by two relaxation processes at low temperatures. At temperatures above 300 K the conductivity contribution dominates, with a small electrode polarization effect. The observed frequency and temperature dependence is qualitatively explained in the framework of a jump relaxation model based on the Debye–Hückel–Falkenhagen theory. At the calorimetrically determined glass transition the measured conductivity is unchanged. This indicates that the mobile charge carriers are not only the counterions themselves but also induced defects.

(Keywords: dielectric properties; glassy polymers; cationic polymerization)

INTRODUCTION

Crosslinked epoxide–amine addition polymers have been used for decades as adhesives, and as components for laminates, composites, etc., since they have good mechanical and thermal properties. The possibility of linear epoxide–amine addition polymerization of diepoxides with primary monoamines opens a way to synthesize soluble high molecular weight polymers[2–4]. These polymers are able to undergo a number of polymer analogous reactions, such as O-acetylation[3], oxidation reactions[3] and N-alkylation[1]. In this 'N-alkylation' new glassy cationic epoxide–amine polymers are synthesized. Cast from dimethylformamide solution they form films with good adhesion on glassy and metallic surfaces as well as self supporting foils with high transparency. The samples used in this study are listed in *Table 1*.

The dielectric properties of these ion-containing polymers and hence their conductivity are only briefly explored. By employing broadband dielectric spectroscopy the frequency and temperature dependence of the complex dielectric function is measured. This enables the underlying mechanisms of charge transport to be investigated and the influence of the chemical structure to be studied by varying the alkyl groups and/or the type of counterions.

EXPERIMENTAL

Sample synthesis is described elsewhere[1–4]. In brief, sample 2 was prepared by dissolving an addition polymer (6.50 g, 14.52 mmol) from 2,2-bis/4-(2,3-epoxy-propoxy)phenyl/propane and benzylamine [M_n(v.p.o.) = 18 800] in 2-methoxyethanol (100 ml) and refluxing for 8 h together with benzyl chloride (18.32 g, 145.20 mmol). The solvent was then distilled. The polymer was dissolved in methanol, precipitated in hexane, isolated and dried *in vacuo* at 10 Pa and 80°C for 8 h.

Analysis for $(C_{35}H_{40}ClNO_4)_n$. Calculated: C, 73.27; H, 7.03; Cl, 6.11; N, 2.44%. Found: C, 72.93; H, 7.02; Cl, 6.96; N, 3.09% (glass transition temperature, $T_g = 90.8°C$; $T_f = 144–153°C$).

In the same way, three further samples, samples 1, 4 and 5, were prepared. Sample 3 was obtained by anion exchange of Cl^- by $ZnBr^{2-}$; sample 2 was dissolved in methanol. A solution of K_2ZnBr_4 in methanol was dropped into the polymer solution and stirred for 1 h.

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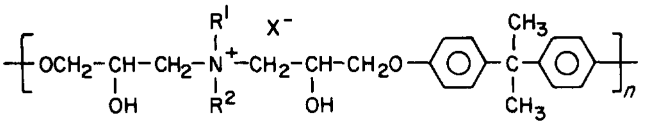
Table 1 Epoxide–amine addition polymers used



Sample	R^1	R^2	X^-	T_g (K)
1	$C_6H_5CH_2$	$C_6H_5CH_2$	Br^-	366.2
2	$C_6H_5CH_2$	$C_6H_5CH_2$	Cl^-	364.0
3	$C_6H_5CH_2$	$C_6H_5CH_2$	$ZnBr_4^{2-}$	347.2
4	$C_6H_5CH_2$	CH_3	I^-	368.5
5	$HOCH_2CH_2$	$CH_3CH_2CH_2CH_2$	Br^-	360.2

The solution was filtered and the polymer precipitated by dropping the solution in hexane. Residual solvents and water were eliminated by drying the samples at 0.1 Pa and 80°C for 24 h. The samples are not hygroscopic.

For the dielectric measurements (10^2–10^7 Hz) an impedance analyser (HP 4192 A) was employed. For the measurements the sample was kept between two condenser plates separated by 50 μm; the separation was maintained by three pieces of fused silica (area ≈ 2 mm^2).

The measurement system used a custom-made cryostat, which allowed the sample temperature to be adjusted between 100 K and 500 K by using a temperature-controlled nitrogen gas jet (stability ± 0.02 K measured over 300 s). The sample temperature was measured with a platinum temperature sensor mounted in one of the condenser plates (temperature resolution ± 0.01 K). For details see references 5 and 6. The experimental accuracy was $\pm 2\%$ and $\pm 5\%$, respectively, for the real (ε') and imaginary (ε'') parts of the complex dielectric function.

RESULTS AND DISCUSSION

The dielectric properties of the cationic polymers under study are dominated by a strong conductivity contribution (*Figure 1*). This gives rise to a steep increase in both ε' and ε'' of the complex dielectric function $\varepsilon^*(\omega, T)$ with decreasing frequency and increasing temperature. The fact that ε' shows a similar frequency and temperature dependence proves that the charge carriers involved in the charge transport are not free (like electrons in a metal). Further conclusions will be discussed later.

At lower temperatures two relaxation processes can be separated (*Figure 2*) which are covered at higher temperatures by the conductivity contribution. Both processes are weak dielectric relaxations and both are strongly broadened. They can be quantitatively analysed by a superposition of the conductivity contribution and the two relaxation processes. For the latter the generalized relaxation function according to Havriliak–Negami[7] is used.

$$\varepsilon''(\omega) = \frac{\sigma_0}{\varepsilon_0}\omega^{(s-1)} + \varepsilon''_{\mathrm{Relax}\,1}(\omega) + \varepsilon''_{\mathrm{Relax}\,2}(\omega) \qquad (1)$$

with

$$\varepsilon''_{\mathrm{Relax}\,i}(\omega) = \mathrm{Im}\left\{\frac{\varepsilon_{Si} - \varepsilon_{\infty i}}{[1 + (i\omega\tau_i)^{\alpha_i}]^{\beta_i}}\right\} \qquad (2)$$

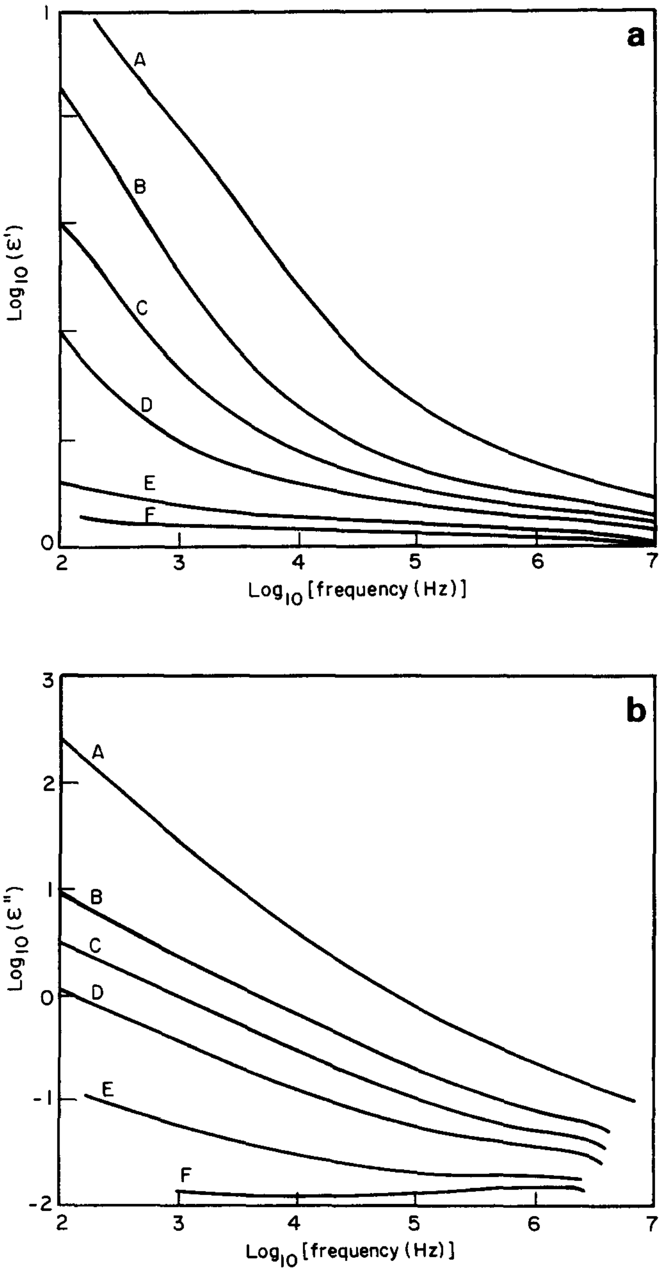


Figure 1 (a) Real ε' and (b) imaginary ε'' parts of the complex dielectric function ε^* *versus* frequency for sample 2 (sample thickness $= 50 \pm 1$ μm) at different temperatures: (A) 379.3; (B) 361.1; (C) 352.6; (D) 343.8; (E) 325.9; (F) 289.5 K

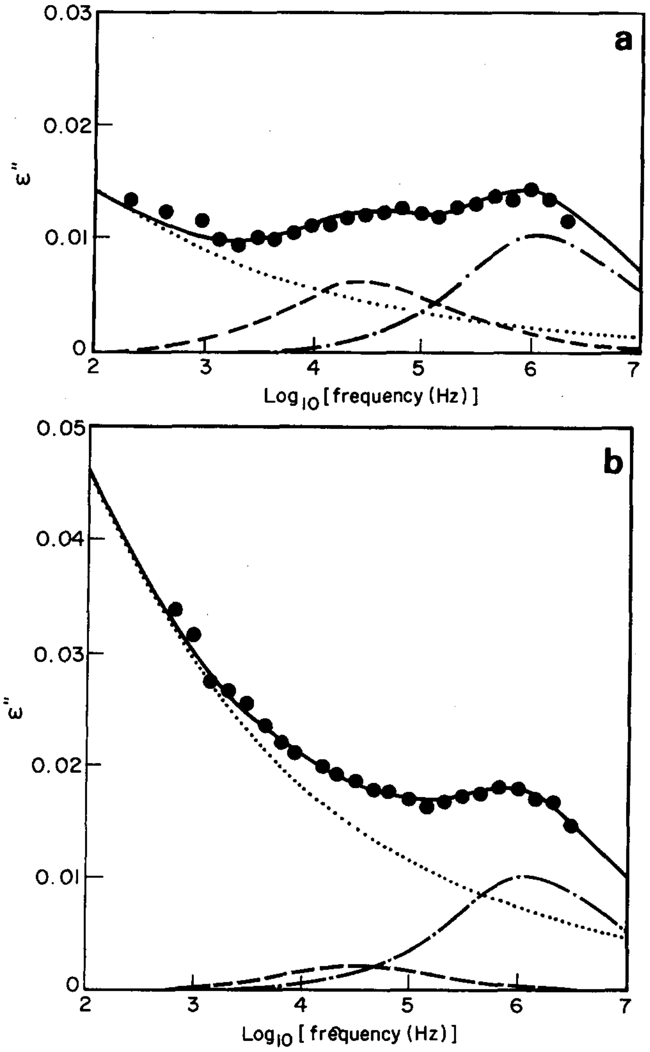


Figure 2 (a) Separation of the conductivity contribution (···) and the two relaxation processes (– –, – ·) according to equation (1), for sample 2 (sample thickness = 50 ± 1 μm). Temperature = 217.0 K. (b) As for (a) but at a temperature = 316.8 K

where σ_0 is a strongly temperature-dependent factor describing the thermal activation of the charge transport, s is a constant with values between 0.5 and 1 being characteristic for hopping conduction[8], the constants ε_{S_i} and $\varepsilon_{\infty i}$ are the values of ε' at the low frequency and high frequency side of the relaxation processes, respectively, and α_i and β_i are constants that determine the width and asymmetry of the relaxation processes ($i = 1, 2$).

The molecular assignment of the relaxation processes is only tentatively possible. The high frequency process in *Figure 2* is assigned to a local mode motion of the ethylene group of the polymeric backbone, which is also known as γ-relaxation[6]. Such a local motion alone would of course not be dielectrically active because no dipole moment is involved. However, the fact that the movement of the ethylene group is transmitted to some extent to the polar ammonium group makes the γ-relaxation dielectrically observable. A similar process was found by Tsutsui *et al.*[9,10] in glassy ionenes using dynamical mechanical spectroscopy. The low frequency process in *Figure 2* is tentatively assigned to a relaxation of the hydroxy group of the polymeric backbone. To confirm this a structural variation of the polymeric backbone would be necessary.

To examine how strongly electrode polarization[11] contributes to the complex dielectric function an Argand representation of the complex impedance $\hat{Z}$ is used (*Figure 3*), $\hat{Z} = Z' + iZ''$, with

$$Z' = \frac{1}{\omega C_0}\left(\frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2}\right) \tag{3a}$$

$$Z'' = \frac{1}{\omega C_0}\left(\frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}\right) \tag{3b}$$

where C_0 is the capacitance of the empty condenser. In the Argand representation electrode polarization causes deviations on the low frequency side[11] which become more pronounced with increasing temperature and hence increasing mobility and increasing effective number

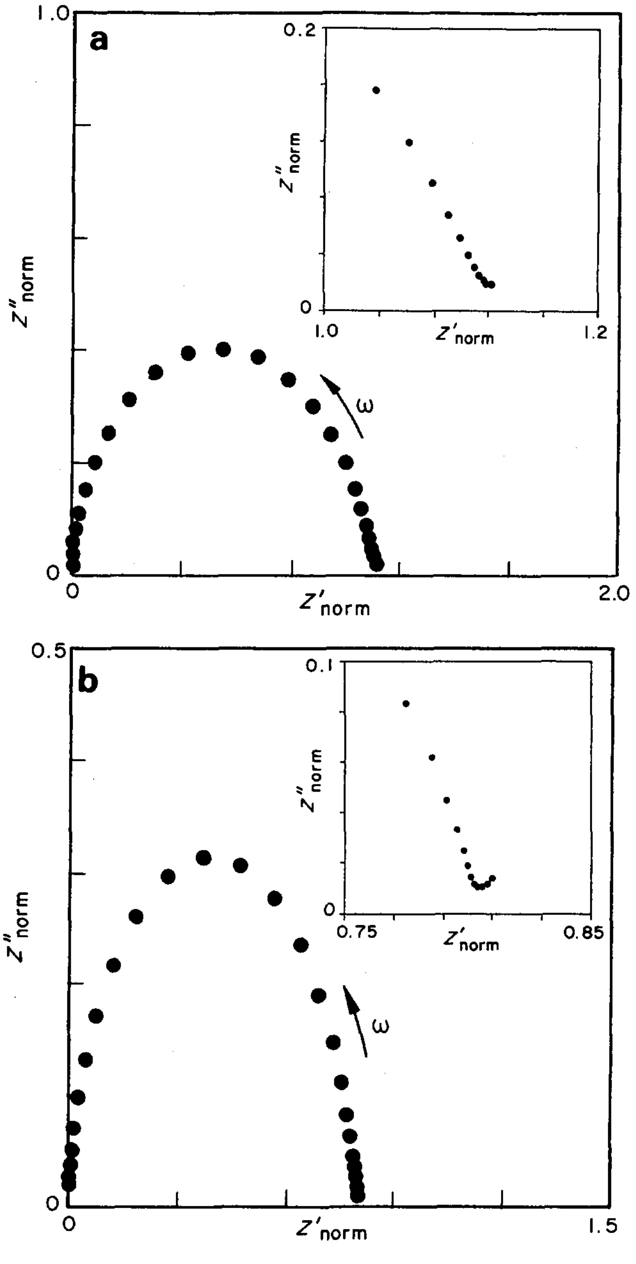


Figure 3 (a) Argand plot of the complex normalized impedance for sample 2 (sample thickness = 50 ± 1 μm). Normalization factor = 20 Ω. Inset: Enlargement of the low frequency part. Temperature = 388.0 K. (b) Argand plot of the normalized impedance. Normalization factor = 10 Ω. Inset: Enlargement of the low frequency part. Temperature = 396.0 K. Other details as in (a)

density of the charge carriers. The insets in *Figures 3a* and *b* show such deviations, which are due to electrode polarization. Thus, the points shown in *Figure 3* at higher frequencies are caused by the bulk conductivity in the sample[11].

The frequency and temperature dependence of the complex conductivity $\sigma^* = \sigma' + i\sigma'' = i\varepsilon_0\omega\varepsilon^*$ (where ε_0 is the permittivity of free space) is typical (*Figure 4*) for solid electrolytes[11–13]. The imaginary part of the conductivity (*Figure 4b*) shows the influence of electrode polarization at low frequencies. The following qualitative features can be summarized:

1. The real part of the conductivity increases with increasing frequency and temperature.

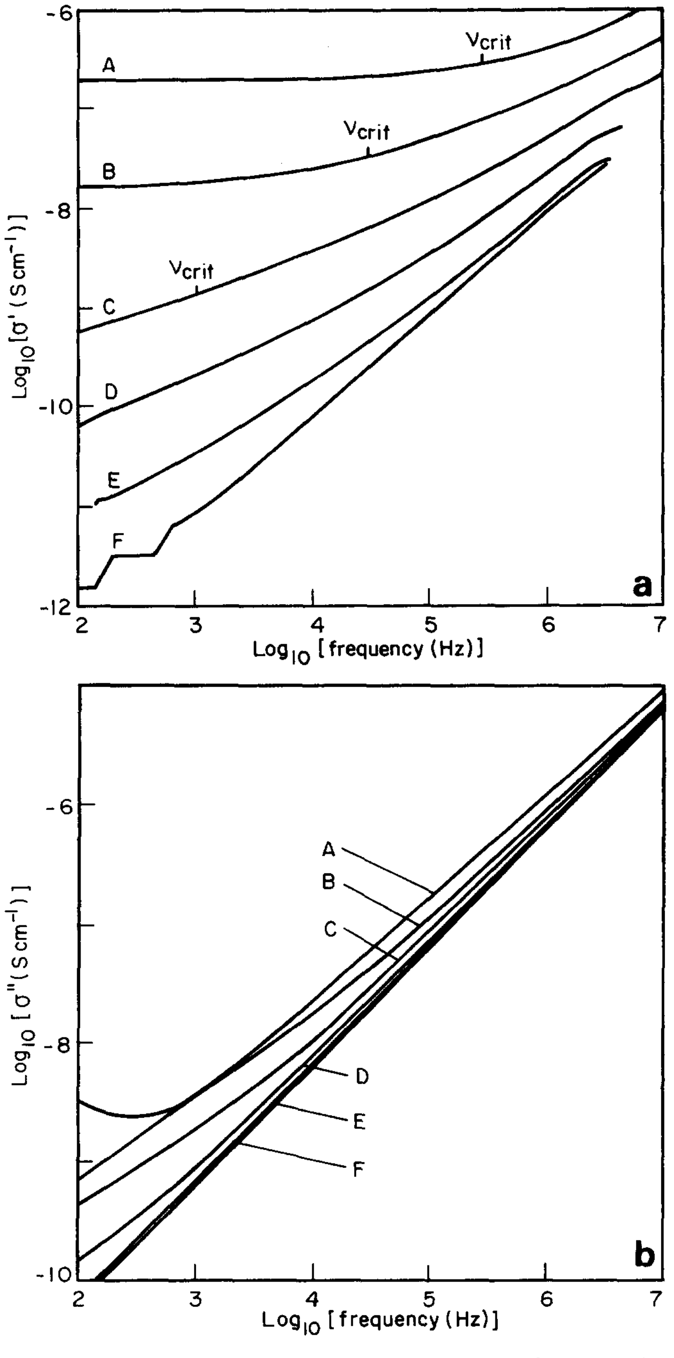


Figure 4 (a) Real σ' and (b) imaginary σ'' parts of the complex conductivity *versus* frequency for sample 2 (sample thickness = 50 ± 1 μm) at different temperatures: (A) 396.2; (B) 379.3; (C) 361.1; (D) 343.8; (E) 325.8; (F) 289.5 K

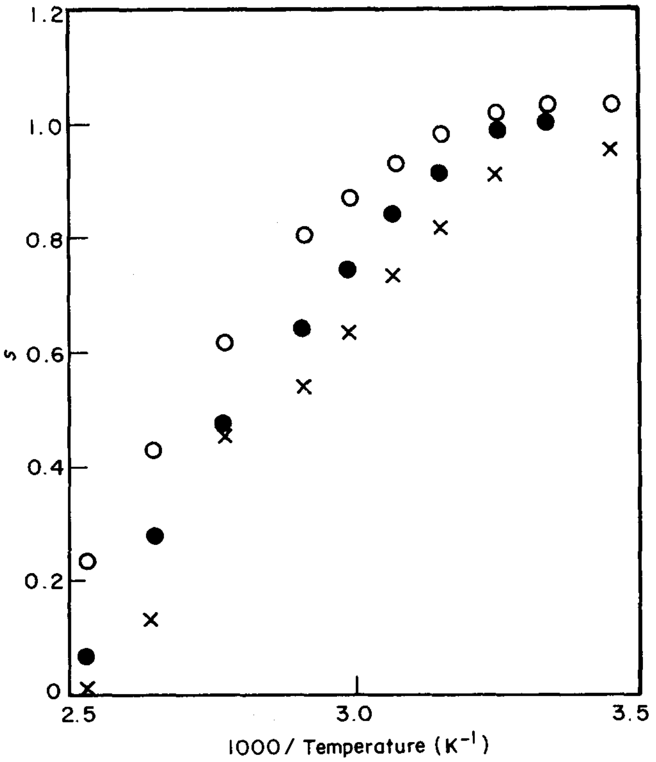


Figure 5 Parameter s according to equation (2) *versus* inverse temperature for sample 2 at different frequencies: (×): 10^3; (●) 10^4; (○) 10^5 Hz

2. For high temperatures the conductivity is almost constant at low frequencies but increases at the critical frequency ν_{crit} where the change of the slope *versus* frequency is maximal (*Figure 4a*).
3. This ν_{crit} shifts to lower values with decreasing temperature.
4. Above ν_{crit} the frequency dependence of the conductivity is proportional to ω^s with $0 \leq s < 1$.
5. At low temperature the real part of the conductivity σ' is proportional to ω^s with $s \simeq 1$.
6. The exponent s in the power law $\sigma' \sim \omega^s$ is a function of both frequency and temperature (*Figure 5*). Similar features have been observed in inorganic glasses as well[13].

At the calorimetrically determined T_g the measured conductivity does not show a discontinuity (*Figure 6*). Similar results were obtained for other ion-containing polymers[6].

The underlying mechanism of charge transport is still a controversial topic[14–19]. Several microscopic models describe the above-mentioned qualitative features of the frequency and temperature dependence of the conductivity:

1. The diffusion-controlled relaxation model[20], which does not assume a distribution of relaxation times as often invoked to explain frequency-dependent relaxation data.
2. An effective medium theory of the motion of ions and/or defects in an amorphous matrix based on a hopping model with randomly distributed sites and activation energies[21,22].
3. The jump relaxation model[23,24] in which a dynamical cage surrounding an ion is introduced – in analogy to the Debye–Hückel–Falkenhagen theory[25,26]. The

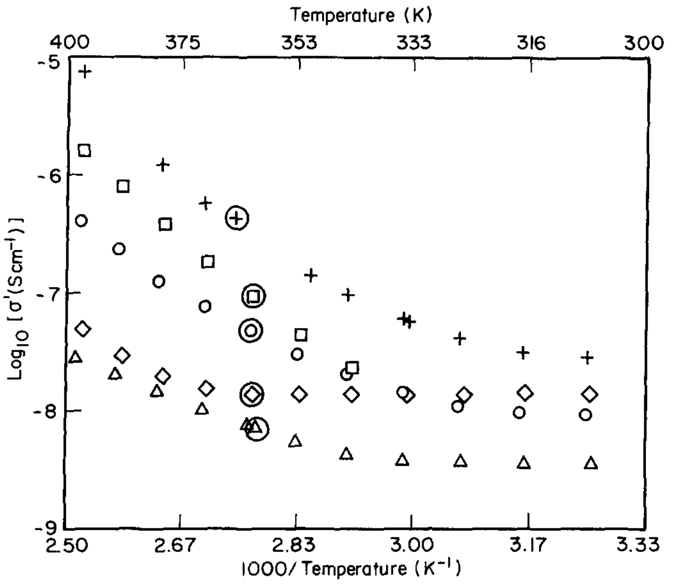


Figure 6 Real part σ' of the complex conductivity of 10^6 Hz *versus* inverse temperature for different types of counterions and different substituents of the polymer matrix as indicated in *Table 1*. The inverse of the T_g is indicated by a large open circle: (◇) sample 1; (○) sample 2; (□) sample 3; (+) sample 4; (△) sample 5

hopping motion of the mobile charged defects is strongly influenced by their mutual repulsive interaction and therefore, their jump diffusion is not a random process. Instead, correlated forward–backward hopping sequences are the elementary step of jump relaxation. In Monte–Carlo simulations[27] for diffusion of charged particles in structurally disordered lattices similar forward–backward correlations were observed leading to power-law behaviour of the relevant transport quantities of intermediate time and frequency scales.

Based on the above experimental data it is not justified to give a preference to any one model.

CONCLUSIONS

The dielectric properties of glassy cationic epoxide–amine addition polymers were measured in the frequency range of 10^2–10^7 Hz and at temperatures between 100 K and 400 K. Besides two weak relaxation processes a strong conductivity contribution is observed. Its frequency and temperature dependence can be qualitatively described by several theoretical approaches for the mechanisms of ionic charge transport in disordered systems. At the T_g the measured conductivity does not show any discontinuity.

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