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Viscosity of salt-in-polymer solutions near the glass transition temperature by penetrometry, and pseudo-macromolecule behaviour at a critical composition in $NaClO_4$–PPO(4000)

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The first viscosity measurements of pure PPO(4000) and PPO(4000) liquid polymer electrolytes at temperatures in the vicinity of the glass transition temperature are reported. At the lower temperatures, ion pairing effects on the transport coefficients are suppressed, permitting some general trends in the dependence of the Vogel–Tammann–Fulcher (VTF) viscosity equation parameters on the salt concentration to be discerned. These are discussed in terms of ion–polymer interactions. Anomalies are noted at the composition $M/O = 1/30$, where some previous studies have found phase separations and these are particularly striking in the case of $NaClO_4$ solutions for which the VTF equation parameters cannot be reconciled with the observed calorimetric glass transition temperature. The existence of a low temperature thermoplastic (rubbery) domain, is identified and a special chain end linking mechanism, which is optimized in the $NaClO_4$ case, is proposed to account for it. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polymer electrolytes; penetrometry; viscosity near T_g; novel thermoplasticity)

INTRODUCTION

Although polymer and polymer solution viscosities are frequently reported, such studies are rarely made at the high viscosity values characteristic of ordinary liquids at their glass transition temperatures. For the high molecular weight polymers used in practical polymer electrolytes, due to the entanglement phenomenon[1], the shear viscosity remains extremely high at temperatures that are far above the glass transition temperature, T_g, while the *local* viscosity, which controls the ionic conductivity, remains quite low. The local viscosity only becomes very high near T_g. To our knowledge, no data have been reported in the high *local* viscosity regime for salt-in-polymer solutions of either high or low MW polymer constituents.

The behaviour of liquid polymer electrolytes in which the polymer hosts are of low MW (in the pre-entanglement regime) is of interest because viscosity data obtained in the low temperature, high viscosity, regime will be less influenced by the ion pairing effects which dominate the temperature dependence of conductivity and also strongly influence the viscosity at normal temperatures[2]. This is because spectroscopic studies have shown that the ion pair concentrations are minimized at low temperatures[3]. Data acquired in the low temperature regime should, therefore, give clearer information on the salt content dependence and temperature dependence of the ion-solvent interactions. In particular, the role of transient crosslinking by cations, which was left ambiguous in our previous study[2], should be clarified by viscosity measurements made near T_g. Combination of such data with previous measurements will yield a sufficient range of analysable data to reliably test the validity of common multiparameter equations such as the Vogel–Tammann–Fulcher equation for transport properties. Here we report and discuss viscosity measurements of pure poly(propylene glycol) MW 4000, PPO(4000), and PPO(4000) liquid polymer electrolytes containing a variety of dissolved salts, made using a penetrometry technique.

This study also provides an opportunity to examine further a curious discrepancy between our earlier and present studies and those of two other groups[4,5]. Vachon *et al.*[4] recently reported d.s.c. studies of $LiClO_4$ and $NaClO_4$ in PPO 4000 which showed two distinct glass transitions, duplicating the earlier study of Moacanin and Cuddihy[5]. Furthermore, in the case of $NaClO_4$, the solution prepared at higher temperatures separated into two macroscopic phases, the upper of which was rich in PPO[4]. Curiously enough, the lower turbid phase apparently continued to show two glass transitions[5].

Our own solutions, by contrast, remained clear over long periods of standing, and gave viscosity data which did not depend on time, regardless of the temperature of

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study. However, as the present work emphasizes, compositions in the range where phase separation, microscopic or macroscopic, has been reported[4,5] do yield very unusual temperature dependences. We will discuss this interesting difference, its possible origins, and its relation to other phenomena after presenting the results of the present study.

EXPERIMENTAL

The salts used in this work were $LiClO_4$ (Aldrich reagent grade), $NaClO_4$ (Aldrich reagent grade), $NaCF_3SO_3$ (Alfa reagent grade), and NaSCN (Alfa reagent grade). PPO(4000) was obtained from the Polyscience Corp. The polydispersity of this product is not specified. The PPO(4000) from Aldrich Co. is stated to be 1.36. The polymer electrolyte solutions were prepared by mixing measured amounts of dried salts with the polymer in a common solvent. Acetonitrile was used as the common solvent in all solutions except NaSCN for which methanol was used. The solvent was then quantitatively removed by vacuum oven drying until constant mass was achieved. Sample preparation has been described in more detail elsewhere[2]. Compositions are expressed as AA/O, where AA and O are the moles of cation and chain oxygen, respectively.

Viscosities in the range 10^9–10^{12} poise found near the glass transition temperature, were measured by penetrometry. Penetrometry involves the monitoring of movement of an incompressible probe as it penetrates into a viscous liquid under constant driving force[6]. For these measurements a Perkin-Elmer Thermomechanical System Model 2, TMS-2, was used. The probe was a quartz hemisphere of radius 0.02″, only a small part of which enters the sample. The constant stress was provided gravitationally by weight from a standard mass kit placed on a weight pan mounted on top of the probe shaft. The sample was placed in a depression of ~2 mm depth in a small copper block. Sub-ambient temperature control to ±0.1°C was obtained using the standard TMS-2 Dewar assembly under the control of the Perkin-Elmer System 4. Unfortunately, instrumental limitations did not permit measurements below ~ −70°C, a range which would have been of interest for pure PPO(4000). The whole TMS-2 instrument was enclosed in a glovebag with N_2 flowing to prevent the sample from picking up moisture during introduction to the copper sample container, or during subsequent measurements.

For hemispherical probes the viscosity may be calculated using the relation[4]

$$\eta = \frac{mt}{kr^{1/2}l^{3/2}} \qquad (1)$$

where η is the viscosity in poise, m is the mass in grams placed on the weight pan minus a correction factor of 1.03 g to be discussed later, t is the time elapsed after initial penetration, r is the radius of the probe in mm, l is the depth of the probe tip penetration, and k is a constant of value 2.7×10^{-11}[4].

A correction factor for the mass was needed because of the buoyancy damping of the probe shaft which floats in a vibration-damping silicone oil reservoir. This correction depends on the probe position and is primarily dependent on the height of the sample holder. Negligible error results from assuming a constant correction factor during collection of a penetration profile (l vs t) since the probe position changes less than 100 μm. Reliable results are then obtained provided this distance is small compared with the sample thickness.

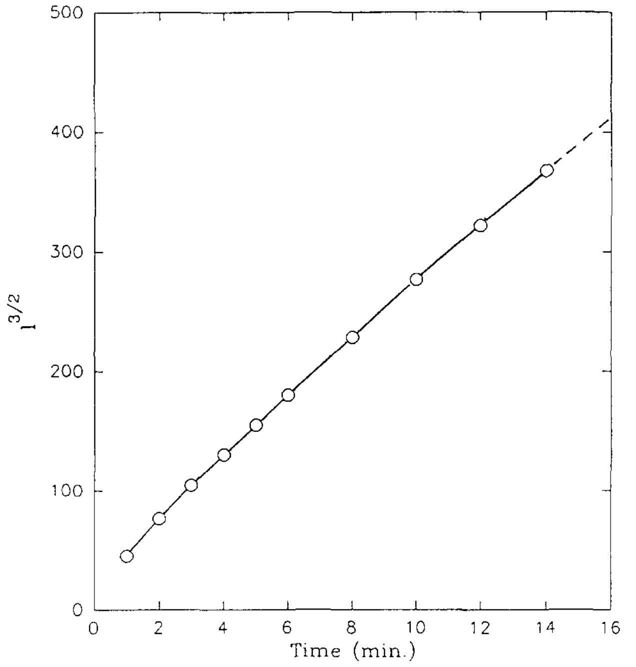

Figure 1 Probe penetration in μm as function of time after contact plotted according to equation (1). The viscosity is inversely proportional to the slope

The technique was checked for consistency with viscosity data for *o*-terphenyl obtained by Laughlin and Uhlmann[7] using a beam bending technique. These had earlier been confirmed here using the TMS-2 in beam bending mode (Tatsumisago, unpublished work)[8]. Preparation of samples for beam bending measurements is very difficult when the substance is liquid at room temperature and it was this difficulty which led us to focus attention on the penetrometry approach. For the latter, only a fresh smooth surface is needed.

As suggested by equation (1), the penetrometry data are plotted as $l^{3/2}$ vs t in order that the viscosity can be extracted from the slope. An example is given in *Figure 1*. In principle this linear regime should extrapolate to the origin, but typically this was not observed. This is probably due to sample surface roughness and to the difficulty of avoiding a small incident momentum of the probe at the initial penetration. However, the results agreed within 15% with those obtained by the beam bending technique. For sub-ambient measurements where viscosity is of order 10^{10} poise, this was considered very satisfactory.

RESULTS

The viscosities near T_g of solutions of various concentrations in the systems PPO(4000)–$NaCF_3SO_3$, PPO(4000)–NaSCN, and PPO(4000)–$NaClO_4$ are shown in *Figures 2–4*, along with spindle viscosity data taken at higher temperatures. For all concentrations below M/O = 1/8, the viscosities measured at low temperatures were smaller than expected from extrapolations of

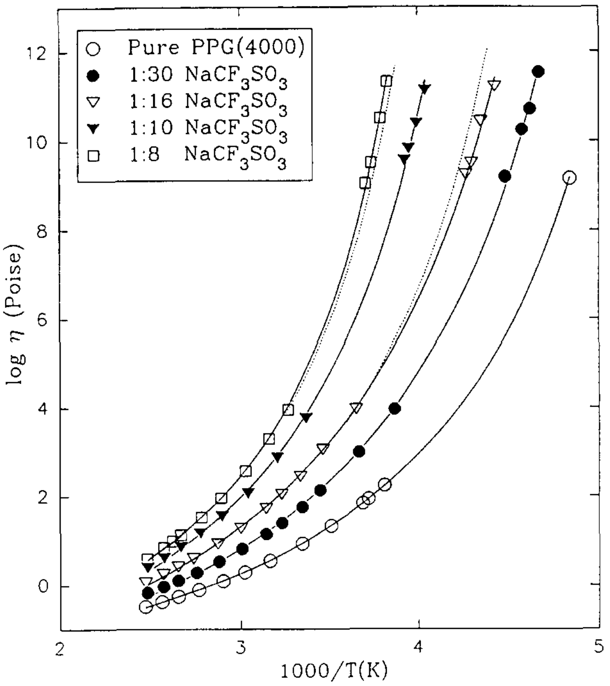

Figure 2 Arrhenius plot of new high viscosity data for NaCF$_3$SO$_3$–PPO4000 solutions, combined with earlier low viscosity data on these solutions from ref. 1. Dotted lines for two cases show the low temperature viscosity predicted from earlier rotating spindle measurement VTF best fit parameters

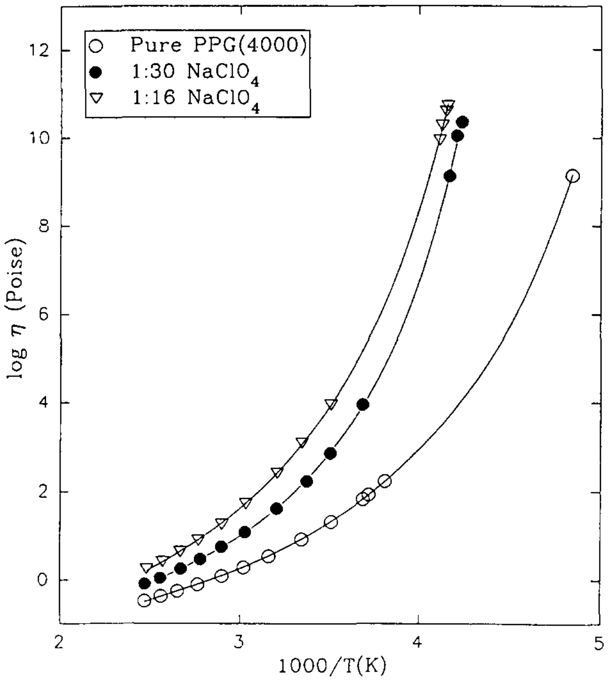

Figure 3 Combination of present and earlier (ref. 1) viscosity data for NaClO$_4$ + PPO(4000) solutions plotted in the Arrhenius representation

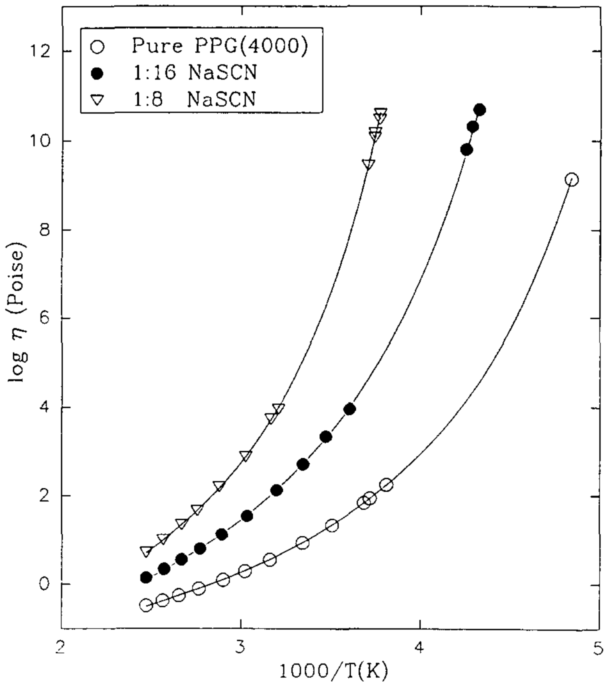

Figure 4 Combinations of present and earlier (ref. 1) range viscosity data for NaSCN PPO(4000) electrolytes in the Arrhenius representation

Table 1 VTF equation parameters for LiClO$_4$–PPO(4000) solution spindle viscosity data

$\eta = AT^{1/2}\exp[DT_o/(T - T_o)]$

M/O	A	D	T_o	Residuals
1/40	1.352e-4	7.148	176.2	3.926e-2
1/30	1.495e-4	6.922	182.2	3.811e-2
1/16	6.569e-5	8.717	182.9	5.065e-2
1/10	1.211e-4	7.082	207.2	2.186e-2
1/8	2.708e-4	5.595	229.4	7.403e-2

Table 2 VTF equation parameters for NaCF$_3$SO$_3$ PPG(4000) spindle viscosity data, and combined spindle and penetrometry data

$\eta = AT^{1/2}\exp[DT_o/(T - T_o)]$

M/O	A	D	T_o	Residuals
1/40	1.962e-4	6.236	178.4	3.553e-2
1/30[a]	1.878e-4	6.164	183.1	5.058e-2
1.30[b]	8.020e-5	7.651	174.4	1.999e-1
1/16[a]	1.465e-4	6.621	190.9	5.113e-2
1/16[b]	5.698e-5	8.321	180.9	2.099e-1
1/10[a]	2.323e-4	5.526	213.7	3.877e-2
1/10[b]	6.046e-5	7.322	202.6	2.622e-1
1/8[a]	1.286e-4	6.222	217.3	2.487e-2
1/8[b]	1.372e-4	5.908	221.0	1.335e-1

[a] Spindle viscosity data
[b] Spindle + penetrometry viscosity data

higher temperature spindle viscosity data based on best fits to the modified Vogel–Tammann–Fulcher (VTF) equation

$$\eta = A_\eta T^{1/2}\exp(DT_o/[T - T_o]) \qquad (2)$$

(A_η, D, and T_o are constants). This is not surprising since, as $T \rightarrow T_g$, the viscosities and relaxation times of glass-forming liquids, particularly fragile liquids, frequently exhibit a tendency to return to Arrhenius behaviour near T_g[7] or at least to change over to lower values of T_o[9,10]. The best-fit parameters for the spindle viscometry data are given in *Tables 1–5*. While all samples other than the 1/8 compositions exhibited the same trend, the magnitude of the deviations depended on the individual system.

Table 3 VTF equation parameters for NaSCN–PPO(4000) viscosity data

$\eta = AT^{1/2}\exp[DT_0/(T - T_0)]$

M/O	A	D	T_0	Residuals
1/40	1.667e-4	6.629	177.1	2.723e-2
1/30	1.418e-4	6.920	179.0	4.940e-2
1/16	1.054e-4	7.403	187.8	5.569e-2
1/10	9.510e-5	7.175	203.9	2.681e-2
1/8	5.697e-5	7.688	210.6	3.612e-2

Table 4 VTF equation parameters for NaClO$_4$–PPO(4000) viscosity data

$\eta = AT^{1/2}\exp[DT_0/(T - T_0)]$

M/O	A	D	T_0	Residuals
1/40	2.265e-4	5.657	188.5	5.754e-2
1/30	3.919e-4	4.430	206.6	2.352e-2
1/16	1.668e-4	6.138	202.5	4.482e-2
1/10	1.516e-4	5.795	222.8	3.600e-2
1/8	1.509e-4	5.738	233.6	2.984e-2

Table 5 VTF equation parameters for LiCF$_3$SO$_3$–PPO(4000) viscosity data

$\eta = AT^{1/2}\exp[DT_0/(T - T_0)]$

M/O	A	D	T_0	Residuals
1/40	2.170e-4	6.418	175.2	2.533e-2
1/30	1.872e-4	6.762	175.9	5.219e-2
1/16	2.100e-4	7.063	182.0	2.696e-2
1/10	2.201e-4	7.152	192.3	1.072e-2
1/8	1.999e-4	7.406	197.6	1.636e-2

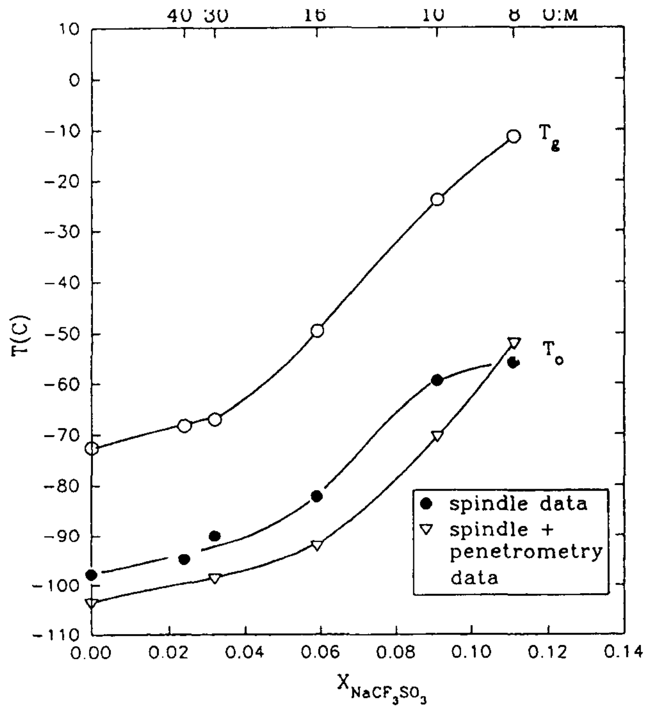

Figure 5 Comparison of composition dependences of the calorimetric glass transition temperature T_g and best-fit T_0 parameters of equation (2) for restricted (ref. 1) and extended data sets, for solutions in the NaCF$_3$SO$_3$–PPO(4000) system

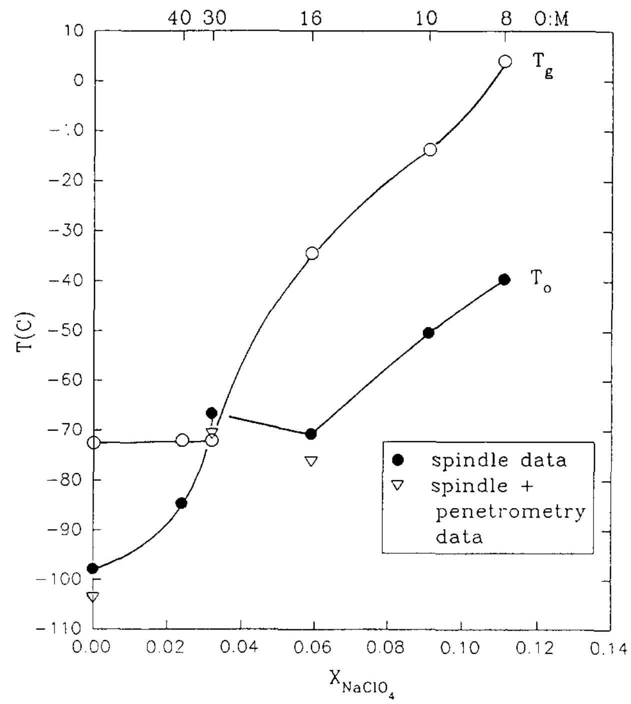

Figure 6 Comparison of composition dependences of the calorimetric glass transition temperature T_g and best-fit T_0 parameters of equation (2) for restricted (ref. 1) and extended data sets, for solutions in the NaClO$_4$–PPO(4000) system. Note inversion of T_0 and T_g values for the composition 1/30

The modification of the VTF parameters which is required when the penetrometry data are included in the analysed data set, differs from solution to solution. It is best displayed graphically by comparing the best fit T_0 parameters for restricted (spindle), and combined, data sets with the experimental glass transition temperatures of the same solutions. These are shown in *Figures 5* and *6*. The extended data set usually requires a lower T_0 than the spindle data alone. Due to the correlation among equation (1) parameters, this means that larger values of D are required by the extended range data set. In the case of the NaCF$_3$SO$_3$ system at the higher concentrations, *Figure 5* shows that the parameters from the extended data sets correlate better with the measured glass transition temperatures than was previously reported[2] on the basis of spindle viscosity data alone. *Figure 6*, however, shows that an unexpected and, at first sight, unphysical relation between T_0 and T_g observed with spindle viscometry data for the NaClO$_4$–PPO4000 system, is confirmed by the penetrometry measurements. The rationalization of this finding will occupy a large part of our discussion.

As noted above, data for the highest salt content solutions, 1/8 are exceptional. The reason that the penetrometry data for the 1/8 compositions do not show the same relationship with the extrapolated spindle viscosity data for the less concentrated (lying above rather than below VTF extrapolations of spindle viscosity data) is probably a result of smaller range of spindle viscosity data for the 1/8 compositions and consequent emphasis of high viscosity domain.

Trends in the 'high' temperature spindle viscosity data were qualitatively preserved at the much lower temperatures of the penetrometry measurements for the 1/30 and 1/16 compositions, as is shown in *Figures 7* and *8*. The

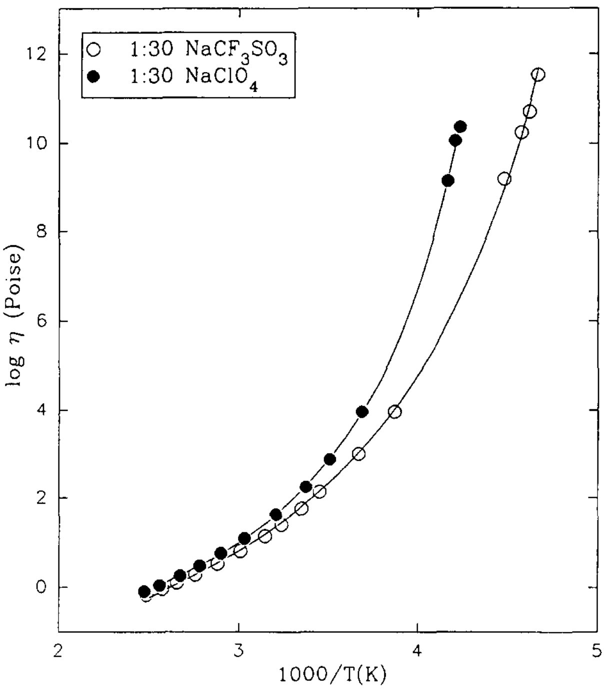

Figure 7 Composition of extended range viscosity data for 1/30 compositions in NaCF$_3$SO$_3$–PPO4000 and NaClO$_4$–PPO4000 systems, in the Arrhenius representation

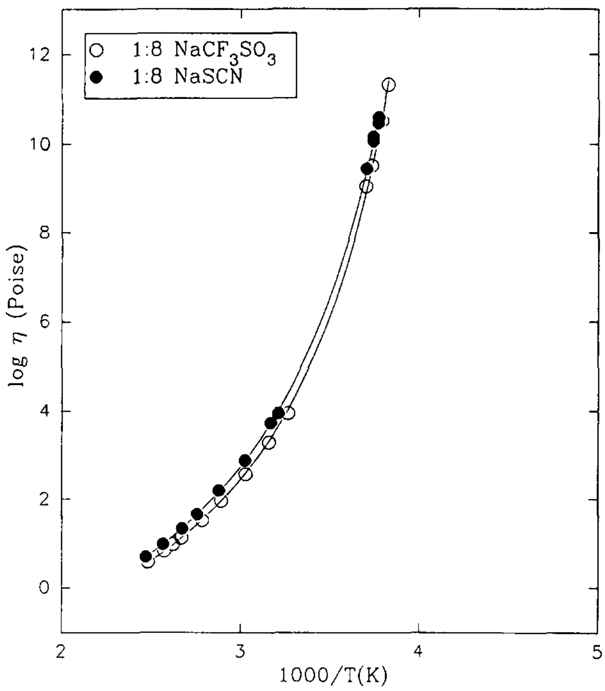

Figure 9 Comparison of extended range viscosity data for 1/8 compositions in PPO4000 solutions of NaCF$_3$SO$_3$ and NaSCN, in the Arrhenius representation

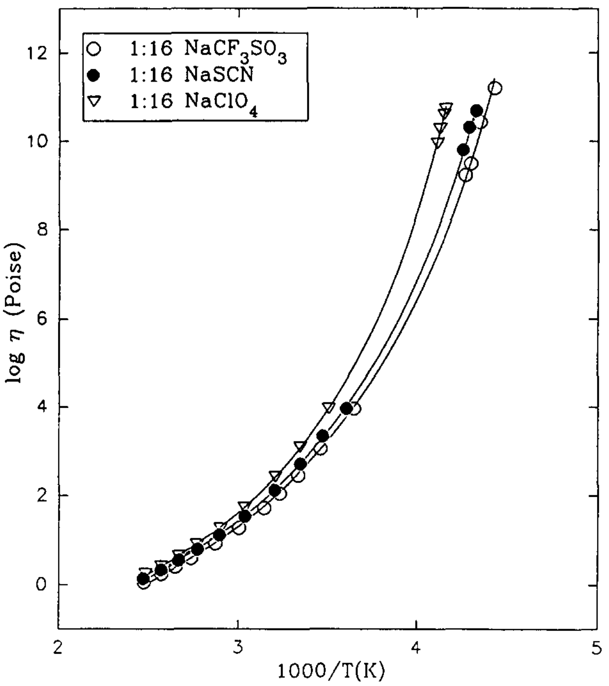

Figure 8 Comparison of extended range viscosity data for 1/16 compositions in PPO4000 solutions of NaCF$_3$SO$_3$, NaSCN and NaClO$_4$, in the Arrhenius representation

differences in viscosity between high and low temperature data at either the 1/30 or 1/16 compositions increased with decreasing temperature. A comparison of the viscosity data for 1/8 NaCF$_3$SO$_3$ and 1/8 NaSCN is shown in *Figure 9*. In this case the viscosities are essentially the same at low temperatures and differ only slightly at higher temperatures. It is likely that the temperature-dependent similarities or dissimilarities of the viscosity data over this extended range are indicative of how comparable the temperature-dependent ion aggregation is in these solutions.

DISCUSSION

Before analysing the effect of salt content on viscosity in this high viscosity regime it is necessary to discuss the results on pure PPO(4000). The low viscosity data for pure PPO(4000) agree well with those of Wang *et al.*[11], and Baur and Stockmayer[12]. Wang *et al.* fitted their data for molecular weights between 400 and 4000 to the common form of the VTF equation

$$\eta = \eta_0 \exp(B/T - T_0) \qquad (3)$$

(which has no temperature term in the pre-exponent) and found that, for PPO polymers of different molecular weight, the B and T_0 parameters were essentially constant while the pre-exponents varied systematically with molecular weight. For PPO(4000), the pre-exponent is 1×10^{-3} P, about an order of magnitude higher than the value of 1×10^{-4} P for PPO(400). The latter is a typical value for a molecular liquid. This difference is a manifestation of the 'polymer effect'. When the molecular weight is very large, e.g. 10^6, the large pre-exponent causes the shear relaxation time to be longer than the enthalpy relaxation time. Then no irreversible flow, only local flow, occurs under shear stress even for T well above T_g and this is the origin of rubbery behaviour in amorphous high polymers above T_g. It is interesting then, and not previously reported, that the viscosity of PPO(4000) measured in the vicinity of T_g leads to an extrapolated viscosity value of $\eta = 10^{11.4}$ at $T = T_g$, a value which is well below the 10^{13} poise commonly associated with the glass transition. This apparent contradiction is due to the fact that PPO(4000), with $D = 5.9$, is intrinsically a rather 'fragile' liquid[13,14], and it

Table 6 Glass transition temperatures, isoviscosity temperatures, and viscosities at the glass transition temperature for PPO4000 and various solutions

Composition	Calorimetric T_g (°C)	T ($\eta = 10^{11.4}$ P) (°C)	Log η ($T = T_g$)
Pure PPO(4000)	−72.5	−72.5	11.39
1/30 $NaClO_4$–PPO(4000)	−72.5	−39.9	$>24^a$
1/30 $NaCF_3SO_3$–PPO(4000)	−67.0	−58.8	$>13.7^a$
1/16 $NaClO_4$–PPO(4000)	−34.4	−34.8	11.27
1/16 $NaCF_3SO_3$–PPO(4000)	−49.6	−47.6	11.91
1/10 $NaCF_3SO_3$–PPO(4000)	−23.9	−27.0	10.71
1/8 $NaCF_3SO_3$–PPO(4000)	−11.4	−12.3	11.16
1/8 NaSCN–PPO(4000)	−14.1	−11.3	12.08

[a] By extrapolation

is typical of fragile liquids (i.e. glass-forming liquids which have low D values) that their viscosities are well below 10^{13} poise at their calorimetric T_g values[15]. This is due either to a decoupling of the viscosity relaxation modes from the structural relaxation modes as T_g is approached[13,14] or to lower values of the high frequency shear modulus which fix the viscosity relative to the relaxation time via the Maxwell equation

$$\eta_s = G_\infty \tau_s \tag{4}$$

where G_∞ is the 'infinite frequency' shear modulus. Thus we find that at MW = 4000 the MW effect (in the pre-exponential term), is not large enough to overcome the fragile liquid effect.

Turning now to the effect of salt additions we compare the temperatures at which the various solutions reach $10^{11.4}$ P [the PPO(4000) value at T_g] with the calorimetric glass transition temperature in *Table 6*. Included in *Table 6* are viscosities at the calorimetric T_g obtained, where necessary, by an Arrhenius extrapolation of the penetrometry data. Extrapolations using equation (2) would give larger values, hence would enhance the effects we now discuss.

For most solutions the temperature at which $\eta = 10^{11.4}$ P is close to the calorimetric T_g. However, the differences in the cases of solutions of M/O = 1/30 are significant. The case of 1/30 $NaClO_4$, in which the viscosity $10^{11.4}$ P is reached 20 K above T_g, is the most striking and will be discussed first. The composition at which this anomaly is observed is essentially the composition at which Vachon *et al.*[4] observed the appearance of the second (higher) glass transition in their study of $NaClO_4$–PPO solutions. Our explanation of the excess viscosity phenomenon requires only a small variation of their picture of the behaviour of solutions in this range. Our explanation involves subnanoscale segregation as opposed to macroscopic phase separation. Firstly, however, we must give evidence that phase separation in our solutions is only incipient, not complete, in our system. The difference must be due to minor differences in polydispersity, average molecular weight, or impurity content, which we will consider later.

The evidence for macroscopic homogeneity in our solutions comes from the detailed behaviour of the viscosity as well as its reproducibility. It requires some detailed discussion.

The first observation which is important for our interpretation of the 1/30 solution is that its equation (2) T_0 parameter is above the well defined calorimetric glass transition temperature for the solution regardless of whether the full range of data, or only the high temperature low viscosity data, are fitted (see *Figure 6*). Since the glass transition is the kinetic manifestation of a thermodynamic transition which would occur at the lower temperature, T_0, if equilibrium could be maintained in the liquid[15,16], this observation implies that the shear relaxation process must be being determined by a mechanism distinct from that controlling the enthalpy relaxation.

An Arrhenius extrapolation of the penetrometry data yields the enormous viscosity of $\sim 10^{24}$ poise at T_g which is more characteristic of high polymers than of most low MW polymer solutions. It implies the existence of a rubbery region above T_g for this solution. Indeed, we were able to demonstrate that in the temperature region between T_g and about 20 K above T_g the penetrometer movement on loading was substantial but was reversed on unloading, as expected for a rubber. Rubbery behaviour usually means macromolecules are present. However, the VTF parameters fitting the viscosity data for this solution do not reveal a large equation (2) pre-exponent as is normally observed in the case of high polymer rubbers. Evidently, there is an additional structural term in the viscosity temperature dependence not present in the enthalpy relaxation temperature dependence which makes the shear relaxation time rise more rapidly than the enthalpy relaxation time with decreasing temperature. The additional structural temperature dependence should then be manifested as an increased fragility (smaller D parameter) in the viscosity which would not be seen in the enthalpy relaxation time or in any other property tied to the local relaxation time (such as the ^{13}C n.m.r. correlation time or the longitudinal relaxation time from light scattering[17]). *Table 4* shows that D indeed falls to the small value of 4.4 at the composition 1/30.

Both the maximum in the anomalous excess viscosity at M/O = 1/30, and the rubbery behaviour associated with it, can be understood if 1/30 is the point in composition where microscopic segmentation sets in for this chain length polymer. We note without comment here that 1/30 is also approximately the ratio of chain ends to in-chain ether oxygens. If ether oxygens are rejected at 1/30 but chain end-OH groups are coordinated by Na^+ more strongly than either, then frustration will result. A statistical number of the chains will be tied to separate Na cations and this will force the incipiently-clustering salt component into a network. Then, as described elsewhere[18] in the interpretation of the more exaggerated case of this phenomenon found for $Mg(ClO_4)_2$ in PPO4000, any additions of $NaClO_4$ will attach to the ionic network centres, reducing the elasticity and increasing the strength of the higher 'salt-complex' glass transition at the expense of the PPO-like transition as seen in the study of Vachon *et al.*[4]

The stronger drive to phase separation seen in the system studied by Vachon *et al.*[4] could have any of several origins. We have noted in the study of $Mg(ClO_4)_2$–PPO4000 rubber-formers[16], that single phase behaviour persists out to $M/O = 1/120$, but that if PPO4000 is replaced with PPO2000 then two separate phases are found for $M/O < 1/20$. The presence of a small fraction of short chain length polymer in Vachon *et al.*'s nominally 4000 MW polymer which they identified[4] could be a critical factor which tips the balance towards macroscopic phase separation in their case.

A second possible source of the different behaviour in the two cases could be a less complete removal of water from our solutions than from theirs. The phase separation phenomenon is believed to originate in the small dielectric constant of PPO (a theoretical prediction[19]), so any factor which would increase the dielectric constant (such as residual water) would decrease the drive to phase separation.

The question immediately arises why this striking difference is not seen as strongly in other polymer salt systems at the same M/O ratio. It must be the result of competitive interactions as discussed by Vachon *et al.*[4] in their explanation of why, in their study, only $NaClO_4$ solutions showed macroscopic phase separation. As might be expected from the weaker phenomena in other systems seen by these workers, we find weaker manifestations of the $NaClO_4$ solution phenomena in the other systems of our study. *Figure 10* shows that a maximum in the decoupling of the viscous and enthalpy relaxation at $M/O = 1/30$ (as determined from extrapolations of spindle viscosity data)[2], is present in every other PPO(4000) electrolyte system examined with the exception of the heavily ion-aggregated $LiCF_3SO_3$–PPO(4000) system[3]. In this case, a maximum in $\eta(T_g)$ occurs at $M/O = 1/16$.

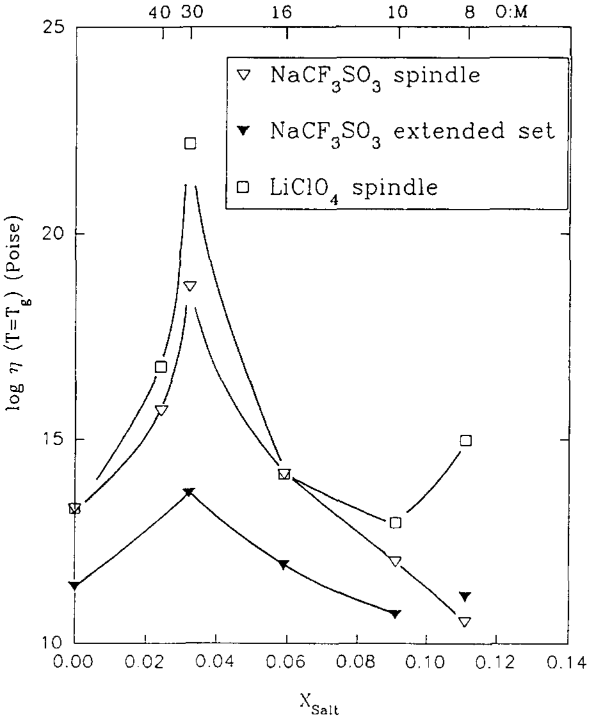

Figure 10 Viscosity at $T = T_g$ for the $NaCF_3SO_3$–PPO(4000) and $LiClO_4$–PPO(4000) systems vs mol fraction salt

For the case of $NaCF_3SO_3$ solutions in *Figure 10* $\eta(T = T_g)$ vs X_{salt} is shown from both extrapolated spindle data and combined spindle plus penetrometry data. It is also shown for $LiClO_4$ solutions using extrapolated spindle viscosity data alone. It is noted that the trend predicted from extrapolations of the spindle viscosity data of $NaCF_3SO_3$ electrolytes at temperatures well above T_g is qualitatively confirmed by the penetrometry data. Moreover, $\eta(T = T_g)$ predicted from spindle viscosity data for 1/30 $LiClO_4$ is quite large although not as large as for 1/30 $NaClO_4$. This supports the previous argument that while the perchlorate anion is important to the rubbery behaviour of 1/30 $NaClO_4$ in this viscosity regime, it is a synergistic effect between Na^+ and ClO_4^- at $M/O = 1/30$ which is responsible for the very pronounced effect in this system. Data based on extrapolations of the spindle viscosity data of the $NaClO_4$ electrolytes near 1/30 cannot be shown in *Figure 10* since for this case the T_0 fitting the viscosity data is greater than T_g (i.e. the VTF equation viscosity diverges at a temperature higher than T_g). The weaker effects seen for the other salts are presumably due to the competition of direct ion pairing with chain end solvation.

There is some structural information available from the X-ray study of the stoichiometric crystalline compound 1/3 $NaClO_4$ PEO[20] which could add refinement to the aforementioned idea. The coordination sphere around Na^+ in 1/3 $NaClO_4$ PEO is three ether oxygens (from contiguous repeat units) and one oxygen from each of two ClO_4^- anions. If preferential inclusion of one chain end -OH in this coordination group were to occur, due to larger dipole of the -OH group, a double ion pair locking mechanism would be provided that would give a three-dimensional net at the stoichiometry 1/30. The special stability of our $NaClO_4$–PPO solution over the lithium analogue would be akin to the special stability of particular crown ether complexes of alkali ions when ion sizes and ligand–ligand separations are optimized.

An obvious test of this scenario would be to replace the hydroxyl end groups with OCH_3 groups, so that the tendency toward preferential end group solvation would be eliminated. However, while such substitutions have been reported for lower molecular weight PPOs[22,22], we have encountered great difficulty in even partially replacing -OH groups of PPO4000 with $-OCH_3$, (or even with -OLi or -ONa groups). On the other hand, the effect of increasing the strength of the interaction by replacing Na^+ by Mg^{2+} or other divalent cations is easily evaluated, and has spectacular results. It yields rubbery substances at ambient temperature, as described elsewhere[18].

At higher salt contents, the glass transition temperature, and estimates of η at T_g, appear to have recovered the normal relationship. This is entirely reasonable since at these higher concentrations the cation solvation is utilizing the backbone ethers to a greater extent, and this would affect η and T_g equally. In the remainder of this discussion we will examine the question of the existence

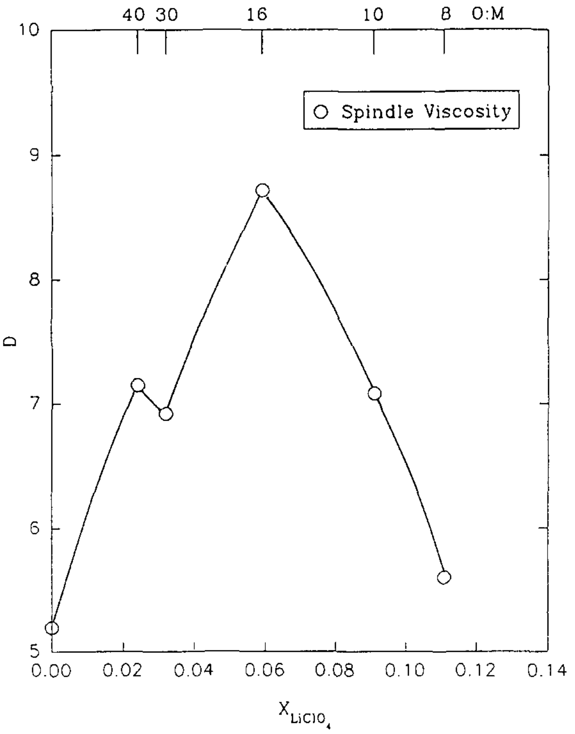

Figure 11 Composition dependence of the best-fit D parameter of equation (2) for restricted[2] viscosities of $LiClO_4$–PPO(4000) solutions

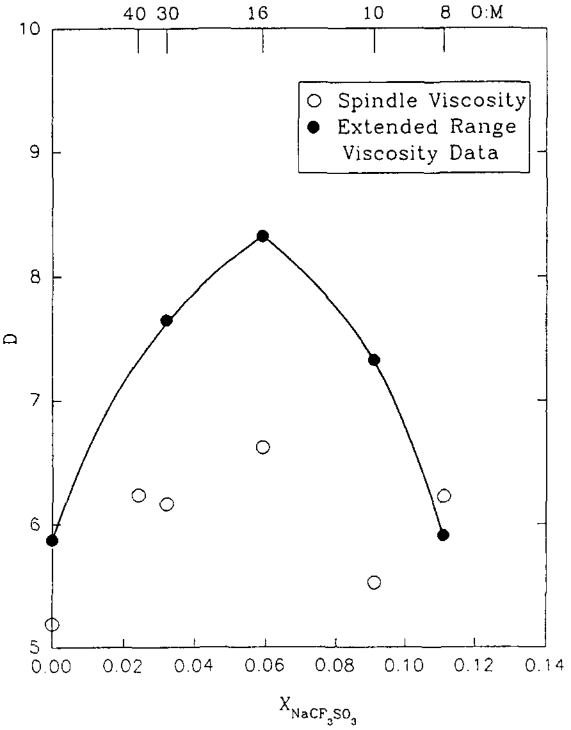

Figure 12 Composition dependence of the best-fit D parameter of equation (2) for restricted[2] and extended range viscosities of $NaCF_3SO_3$–PPO(4000) solutions

of a fragility maximum in the vicinity of $M/O = 1/16$ suggested earlier[2] on the basis of data from the systems $NaCF_3SO_3$–PPO4000, and $LiClO_4$–PPO4000, studied only at lower viscosities in the spindle viscometry range.

The composition dependences of the D parameters (D^{-1} indicates the fragility) are shown in *Figures 11* and *12*. In *Figure 11*, the D parameter for the $LiClO_4$ solutions determined from spindle viscosity date is seen to increase as the salt content increases up to 1/16 (M/O) (with the anomalous local minimum at 1/30 discussed above). It then decreases at higher salt contents. Since $LiClO_4$ solutions are highly dissociated[3,22–24], the initial rise in the D parameter value with increasing salt content was interpreted[2] as due to dissolved cations acting as transient crosslinks to set up a quasi-three dimensional structure, with maximum efficacy at the 1/16 composition. At higher salt contents the return to lower D values was interpreted as a consequence of the increasing coulomb interactions due to the decreasing ionic separations. This led to behaviour approaching that of molten salts and hydrate melts which are known for their low D values[23,25].

The composition dependence of the D parameter for the $NaCF_3SO_3$ system, as anticipated[2], is dependent on whether or not low temperature penetrometry data are included in the fit. Using only the high temperature viscosity data, the D parameter was found[2] to be rather insensitive to composition and this finding is reproduced in *Figure 12*. It is not completely unexpected in view of the fact that these solutions are highly ion-paired at higher temperatures[23,24] and would have fewer free ions for transient crosslinking. However, when the $NaCF_3SO_3$ penetrometry data (which are obtained at temperatures at which these solutions are not highly dissociated) are included in the VTF fits, a composition dependence for the D parameter very similar to that of the $LiClO_4$ polymer electrolytes emerges.

This same pattern seems to exist in the NaSCN viscosity data although the amount of penetrometry data is more limited and the apparent maximum in D at the 1/16 composition is less pronounced. The composition dependence of the D parameter for the $NaClO_4$ electrolytes does not fit this general and attractive interpretation. However, the possible dominance of the end group solvation in 1/30 $NaClO_4$, which results in the unique relationship between T_0 and T_g discussed above, and the codependence of the VTF parameters, accounts for this apparent special case. If the D value for 1/30 $NaClO_4$ is ignored, $D(X_{NaClO_4})$ behaves as in the other cases, although the maximum D value at the 1/16 composition is smaller than in the other PPO(4000) electrolyte systems.

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REFERENCES

1 Ferry, J. D. 'Viscoelastic Properties of Polymers', Wiley, New York
2 McLin, M. G. and Angell, C. A. *J. Phys. Chem.* 1991, **95**, 9464
3 Torell, L. M. and Schantz, S. 'Polymer Electrolyte Reviws—2' (Eds J. R. MacCallum and C. A. Vincent), Elsevier, London, 1989, p. 1
4 Vachon, C., Vasco, M., Perrier, M. and Prud'homme, J. *Macromolecules* 1993, **26**, 4023

5 Moacanin, J. and Cuddihy, E. F. *J. Polym. Sci.* 1966, **14**, 313

6 Douglas, R. W., Armstrong, W. L., Edward, J. P. and Hall, D. *Glass. Technol.* 1965, **6**, 52

7 Laughlin, W. T. and Uhlmann, D. R. *J. Phys. Chem.* 1972, **76**, 2317

8 Tatsumisago, M. and Angell, C. A. in 'Proc. of 30th Glass Meeting', Japan, 1989

9 Dixon, P. K. *Phys. Rev. B* 1990, **42**, 8179

10 Stickel, F., Fischer, E. W. and Schönhals, A. *Phys. Rev. Lett.* 1994, **73**, 2936

11 Wang, C. H., Fytas, G., Lilga, D. and Dorfmuller, T. H. *Macromolecules* 1981, **14**, 1363

12 Baur, M. R. and Stockmayer, W. H. *J. Chem. Phys.* 1965, **43**, 4319

13 Angell, C. A. *J. Non-Cryst. Sol.* 1991, **131–133**, 13

14 Angell, C. A. *J. Phys. Chem. Sol.* 1988, **102**, 205

15 Angell, C. A., Alba, C., Arzimanoglou, A., Böhmer, R., Fan, J., Lu, Q., Sanchez, E., Senapati, H. and Tatsumisago, M. *Am. Inst. Phys. Conf. Proc.* No. 256, 1992, 3

16 Adams, G. H. and Gibbs, J. H. *J. Chem. Phys.* 1965, **43**, 139

17 Angell, C. A., Monnerie, L. and Torell, L. M. *Symp. Mater. Res. Soc.* 1991, **215**, 3

18 Lu, Q., Sanchez, E. and Angell, C. A. *Electrochem. Acta* 1995, **48**, 2239

19 Singh, R. R. and Pitzer, K. S. *J. Chem. Phys.* 1990, **92**, 6775

20 Lightfoot, P., Mehta, M. A. and Bruce, P. G. *J. Mater. Chem.* 1992, **2**, 379

21 Merz, A., *Angew. Chem. Int. Ed.* 1973, **12**, 846

22 Torell, L. M. in 'Handbook of Solid State Batteries and Capacitors' (Ed. M. Z. A. Munshi and P. S. S. Prasad), World Scientific, 1994, p. 270

23 Kakihana, M., Schantz, S. and Torell, L. M. *J. Chem. Phys.* 1990, **92**, 6271

24 Kakihana, M., Schantz, S., Mellander, B. E. and Torell, L. M. in *Proc. 2nd Int. Symp. Polymer Electrolytes*, p. 23

25 Angell, C. A. and Tucker, J. C. *J. Phys. Chem.* 1974, **78**, 278