Effects of Ionic Cross-linking on the Non-exponentiality of the α-relaxation in Metaphosphate Glass Melts as Measured by Dynamic Light Scattering

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Abstract

Photon correlation spectroscopy was conducted on a series of metaphosphate glass melts to measure the liquid's dynamic structure factor near the glass transition and thereby characterize the degree of non-exponentiality in its time decay. Each metaphosphate consists of polymeric chains of $[PO_4]^{-1}$ monomers interspersed by a variety of modifying cations (Ag^+, Ba^2, Ca^{2+}, Sr^{2+}) which can potentially form inter-chain crosslinks via ionic bonding. Our results show that the non-exponentiality of the α-relaxation decreases monotonically with increasing field strength of the cation-oxygen bond.

1. Introduction

Phosphate glasses[1] feature prominently in a range of applications including high thermal expansion materials for glass-metal seals[2], low phonon loss hosts for rare earth ion lasers[3], and active media for promoting bone regeneration in the human body[4]. Phosphate glasses also serve as a model system for examining how the structure of the oxide glass network present in the solid phase influences glass forming dynamics in the liquid[5-8]. In sodium phosphate glasses defined by $(Na_2O)_x(P_2O_5)_{100-x}$ for example, glasses can be successfully formed over a continuous range from x = 0 to nearly x = 67% and display little or no tendency for crystallization in the melt. Across this wide composition range the oxide network undergoes a systematic depolymerization[1]. Starting from P_2O_5 which forms a continuous 3-dimensional network of bridging oxygen (BO) connections between phosphorus atoms wherein each PO_4 tetrahedra has exactly n = 3 bridges, the addition of a modifying cation like Na^+ results in the formation of a non-bridging oxygen (NBO) which lowers the overall bond density of the oxide network. The depolymerization proceeds to the metaphosphate composition (x = 50%) where every tetrahedra has exactly n = 2 bridging oxygens and forms a melt composed of long *polymeric* chains of -$[PO_4]^{-1}$- whose single negative charge is distributed evenly among the 2 remaining non-bridging oxygens of the unit. Beyond the metaphosphate, the addition of more alkali result in shortening of the chains as -$[PO_4]^{-2}$ units begin to appear. Near the pyrophosphate composition (x = 67%) the oxide structure has degraded to an ionic mixture of alkali ions interspersed by mostly PO_4 dimers (i.e., $[P_2O_7]^{4-}$ anions). These changes in oxide structure are well-documented[1] and result in major changes in both the glass transition temperature, T_g, and in the so-called *fragility*[9] of the melt,

$$m = \left.\frac{d\log_{10}\langle\tau\rangle}{d(T_g/T)}\right|_{T\to T_g}, \tag{1}$$

which characterizes how rapidly either the viscosity or the average relaxation time $\langle\tau\rangle$ increases just near T_g.

In the last decade or so, several groups have endeavored to develop models that can predict both T_g and m based on the chemical bond structure of the glass solid. Some have examined the implications of mechanical constraints imposed on atoms by the formation of various bonds in the glass[10,11]. By assigning each bond type a unique temperature above which it no longer functions as a constraint[11], both T_g and fragility in several oxide glasses have been modeled. In an alternative approach[12,13], the fragility of a great many network-forming glasses was shown to depend only on the average bond density or, whenever rigid structural units (e.g., small rings) are present, on a coarse-grained equivalent bond density.

A persistent issue in these models is the question of whether the ionic bonding by the modifying cation counts as either a constraint or contributes to the average bond density since the ionic bond with the oxide network is generally weaker than the covalent BO bonds that comprise the network itself. Zachariasen[14] famously sorted the different cations into either network formers (including Si^{4+}, P^{5+}, B^{3+}) that promote a continuous covalent network of BOs or modifiers (such as Li^+, Na^+, Ca^{2+}) that are added to either polymerize or depolymerize the oxide network. Additionally, his classification includes a group of so-called intermediates (e.g., Al^{3+}, Zn^{2+}) that can function either as network former or modifier depending on the circumstances[15]. In many oxides, small monovalent cations exhibit measurable ionic conduction in the solid that would suggest these cations are fully decoupled from the oxide network and so do not contribute to its overall structural integrity. On the other hand, studies[16,17] of metaphosphates for which a small monovalent cation is replaced by Zn clearly suggest that Zn participates in network formation possibly forming a subnetwork[18] of ZnO_4 tetrahedra in zinc phosphate glasses.

Efforts to answer this question of whether modifying cations participate in the network structure have centered mainly on metaphosphate glasses[7,19-21]. Metaphosphate melts can be obtained with a wide variety of interstitial cations ranging from monovalent to trivalent while the basic phosphate structure consisting of chains of $-[PO_4]^{-1}-$ tetrahedra remains unaltered and isostatic. Several researchers have reported correlations of both the glass transition temperature[19] and the fragility[7,20,21] with changes in the *field strength* of the modifying cation. The field strength (expressed alternately as an energy, Z/d or as a force, Z/d^2) is the ratio of the cation valence Z to its center-to-center separation from the oxygen atom, d, and is an obvious measure of the strength of the ionic bond being formed. Generally, the T_g increases and the fragility decreases with increasing field strength both of which suggest increased bonding of the network.

However, another important aspect of the dynamics in glass forming melts is the *non-exponentiality* of the primary viscoelastic relaxation also known as the α-relaxation[22,23]. Broadband dielectric studies conducted on multiple simple molecular liquids[24,25] and conventional hydrocarbon-based polymers[25,26] reveal the α-relaxation as a peak in the dielectric loss as a function of frequency that shifts to lower frequencies with cooling. The width of this peak is often broader than that (1.14 decades) of a traditional Debye process involving an exponential time decay[26], and the non-exponential relaxation is commonly associated with a KWW or "stretched" exponential decay of the form

$$exp\left\{-(t/\tau)^{\beta}\right\}, \tag{2}$$

where the stretching exponent β ranges from 0.2 to 1.

This same primary relaxation can also be monitored in the time domain using photon correlation spectroscopy (PCS) which measures the dynamic structure factor of the liquid via fluctuations in the scattering intensity[27]. An advantage to the PCS technique is that it can monitor the α-relaxation even in ion-conducting materials for which dielectric spectroscopy is severely compromised by a competing dielectric loss due to mobile charges[25]. Here we present results of a photon correlation study conducted on four metaphosphate glass melts which are combined with previous PCS studies to show that viscous relaxation in these metaphosphate melts becomes less non-exponential (i.e., β increases) as the field strength of the modifying cation increases.

2. Experimental

2.1 Sample Preparation

$Ca(PO_3)_2$, $Ba(PO_3)_2$ and $Sr(PO_3)_2$ were each prepared by reacting the respective alkaline earth carbonate with $NH_4H_2PO_4$ (99.999%) in a porcelain evaporating dish at 500 C. Batch was added to the dish in small amounts to avoid foam over and then baked until the final weight matched calculations to within 0.5%. The resulting powder was later remelted in a silica ampoule (6 mm ID x 8 mm OD) that served as the light scattering cell. $AgPO_3$ was similarly prepared by reacting $AgNO_3$ (99.9995%) with $NH_4H_2PO_4$ in a silica crucible. After calcining for 17 hours at 350 C, the yellow-colored melt was heated to 500 C and poured to form slender rods (approximately 4 mm in diameter) that could be remelted in the light scattering cell. Whenever possible high purity materials were chosen to reduce the presence of small insoluble particulates that could contribute unwanted light scattering. In all instances, glass melts were degassed under vacuum (200 mTorr) to remove bubbles prior to measurements.

2.2 Photon Correlation Spectroscopy

After melting, samples were transferred to an optical oven whose temperature could be controlled to ± 0.2 C. Vertically polarized light (532 nm, Coherent Verdi 5) was focused into the sample and the light scattered at 90 degrees was imaged onto a 50 micron pinhole and then allowed to diffract over some 40 cm distance before impinging on the photoactive surface of a photomultiplier tube. The resulting photopulses were discriminated and digitized before input into a commercial autocorrelator which computed the intensity-intensity autocorrelation function (ACF),

$$C(t) = \frac{\langle I(t\prime)I(t\prime+t)\rangle}{\langle I(t\prime)\rangle^2} = 1 + A_{COH}|S(q,t)|^2, \qquad (3)$$

which, in the absence of any extraneous scattering, is directly related to the dynamic structure factor, $S(q,t)$, of the melt. Here the coherence factor, A_{COH} = 0.80, is a calibrated constant dependent on the pinhole size and diffraction distance described above. In practice however, the low levels of intrinsic light scattering from the metaphosphate melts made unwanted scattering from diffusing particulates a consideration in the data analysis. Whenever present, the sporadic intensity fluctuations from these slowly diffusing particulates resulted in an additional decay to the ACF at times much longer than the viscoelastic α-relaxation. Given this large time separation, the artifact could be treated as merely an additional contribution to the baseline and so ACFs were generally fit to

$$C(t) = 1 + B + A_{COH}\left|Aexp\left[-(t/\tau)^{\beta}\right]\right|^{2}, \tag{4}$$

where A is the amplitude of the α-relaxation and B is the additional contribution to the baseline. In all instances the ratio of B/A was less than 20 %.

3. Results

Autocorrelation functions were obtained over a range of selected temperatures above T_g for each of the metaphosphate glass melts in our study. As an example, the ACF for $AgPO_3$ obtained near 200 C is presented in Fig. 1 and shows a very gradual decay transpiring over several decades in time.

Included in the figure is a typical fit to Eq. (4) illustrating how the stretched exponential (with a stretching exponent of β = 0.38 in this instance) provides an excellent description of the time decay over a broad time window of more than eight decades. In all instances the relaxation time, τ, increased with decreasing temperature, and as seen by examination of Fig. 2, the rates of increase in τ with decreasing temperature are not alike. The relaxation time increases far more rapidly for $AgPO_3$ than it does for the other three divalent melts and indicates that this monovalent melt is considerably more fragile. The glass transition temperature is conventionally defined as that temperature where the average relaxation time, $\langle\tau\rangle = \frac{\Gamma(1/\beta)}{\beta}\tau$, approaches 100 seconds and was determined by extrapolation in Arrhenius graphs of $\log_{10}\langle\tau\rangle$ plotted against inverse temperature. This was then used to rescale the abscissa to inverse temperature scaled by the glass transition temperature from which the fragility index could be determined as defined by Eq. (1). Results for T_g and the fragility are summarized in Table 1.

Table 1: Analysis of monovalent and divalent metaphosphate melts obtained from PCS.

Modifier	T_g (C)	m	β_{AVG}	d (Å) [20]
Ag	184	85 (± 5)	0.37 (± 0.05)	2.36
Na	275	83 (± 5)	0.43 (± 0.05)	2.38
Li	340	90 (± 5)	0.50 (± 0.04)	2.03
Ba	493	46 (± 3)	0.52 (± 0.04)	2.79
Sr	524	48 (± 5)	0.51 (± 0.07)	2.55
Ca	570	45 (± 3)	0.56 (± 0.06)	2.39
Zn	450	30 (± 2)	0.60 (± 0.02)	1.95

Results for the stretching parameter are presented in Fig. 3 where values for several metaphosphates have been plotted against the relaxation time. Data for $Ca(PO_3)_2$ and $Sr(PO_3)_2$ are very similar to those of the $Ba(PO_3)_2$ shown and have been omitted for greater clarity. Included also in the figure are results for $LiPO_3$, $NaPO_3$ and $Zn(PO_3)_2$ that were obtained previously[17, 28]. By and large, the stretching parameter is independent of the temperature for relaxation times longer than 10 milliseconds and indicates that thermorheological simplicity[25,26] (wherein time-temperature superposition of relaxation spectra can be performed) applies close to the glass transition. Moreover, the average value of the parameter near T_g displays clear variations depending on the type of modifying cation. For $Zn(PO_3)_2$ the β_{AVG} is 0.60 while at the opposite extreme, β_{AVG} of $AgPO_3$ is 0.37. Values of β_{AVG} are summarized in Table 1 and are plotted in Fig. 4 as a function of the field strength (force) of the modifying cation. A well-defined correlation is evident wherein the exponent decreases with decreasing field strength.

A peculiar feature of the stretching exponent noted in Fig. 3 is the somewhat abrupt decrease that happens only for the monovalent cations as the relaxation time decreases below about 10 milliseconds. This feature was particularly pronounced in the current investigation of $AgPO_3$ and led to closer examination of older data sets[28,29] for $LiPO_3$ and $NaPO_3$ which also appear to exhibit a similar decrease in β in the same vicinity to values as low as β = 0.22.

Careful examination of the curve fitting for $AgPO_3$ in this vicinity confirmed that the enhanced stretching of the decay is not an artifact of the ACF having shifted too far beyond the lower edge of our experimental time window. Attempts to force fit the ACF using a larger exponent were deemed inferior and so we conclude that for monovalent melts the decay in indeed becoming more stretched with increasing temperature.

4. Discussion

Conventional linear polymers like poly(styrene) consist of long chains of repeated hydrocarbon units that are partially entangled with other chains to form an amorphous melt. The viscous α-relaxation in these materials is thought to be associated with cooperative segmental motion of the chains[30,31] wherein coupling to neighboring chains takes place only through van der Waals interactions. This weak inter-chain interaction results in materials with glass transitions typically below 100 C and fragilities in excess m = 100[31,32]. In addition, studies reveal an α-relaxation in conventional polymers that is considerably non-exponential with $\beta\left(T_g\right)$ ranging from 0.24 to 0.55 near the glass transition temperature[25,31,32].

In similar fashion, the metaphosphate melts consist of chains of repeated PO_4 tetrahedra ranging from 50 to 100 units. The viscous relaxation is likewise associated with segmental motions, but given their higher glass transition temperatures, one cannot rule out possible rearrangements associated with intra-chain P-O bond breaking[33] which can become more prominent at temperatures above 430 C, the T_g of P_2O_5[17]. A key difference in the metaphosphate melts is the potential role of inter-chain crosslinking that could be provided by the modifying cation. Each PO_4 tetrahedron has two bridging oxygens that form the P-O-P polymer backbone and two negatively charged non-bridging oxygens that can potentially form ionic bonds with the interstitial cation.

Several groups have suggested that the field strength and/or the cation-oxygen coordination number appear to determine important glass properties such as the glass transition temperature and the melt fragility[7,17,19-21]. In our present investigation we see similar trends in both these properties - the T_g generally increases and fragility decreases with increasing cation-oxygen bond strength - all in good agreement with previous studies. Unique to the present study, however, is the evolution of the stretching exponent that increases with increasing cation field strength. In $AgPO_3$, for which the field strength is lowest, we find the T_g, fragility and stretching exponent all approaching those extreme values reported for some conventional (hydrocarbon) polymers for which inter-chain crosslinking is limited only to van der Waal interactions.

Current opinion[34,35] as to the source of the non-exponential relaxation favors *heterogeneity* models for which the relaxation is a collective result of many different regions relaxing with a distribution of relaxation times (DRT): some fast and others slow. The width of the distribution (FWHM in decades) needed to produce the stretched decay with exponent β can be estimated[32] as W = 1.14/ β. Thus, the increase of β with cation field strength seen in Fig. 4 would imply a systematic narrowing of the distribution of relaxation times (DRTs) as stronger crosslinks are introduced between phosphate chains. We speculate that the narrowing may be expected as the crosslinks serve to constrict and limit the segmental modes of motion of the chains, effectively stiffening the structure and thus likely reducing the variety of relaxation rates. At the one extreme of $AgPO_3$ we find β_{AVG} similar to the $\beta\left(T_g\right)$ of several conventional polymers for which ionic crosslinking is absent. At the opposite extreme, $Zn(PO_3)_2$ displays β_{AVG} ≈ $\beta\left(T_g\right)$ seen in many base oxide glasses[36] such as P_2O_5 and GeO_2 which form a continuous 3-dimensional network of covalently bonded atoms in which local relaxations are dominated by bond "scission-renewal" events[33].

Lastly, the peculiar transition in $\beta(\tau)$ seen for only the monovalent cations (Ag, Na and Li) in Fig. 3 deserves comment. This decrease in $\beta(\tau)$ to values near or below 0.25 occurring as τ decreases below about 10 milliseconds would indicate a rapid broadening of the DRTs to widths of four or more decades. At these higher temperatures, the DRTs of these melts match those found in some non-crosslinking, non-ionic conventional polymers[32,39]. The temperature dependent β would also imply the absence of thermorheological simplicity (TRS) in which relaxation decay functions preserve their shape and can be collapsed together by simple time-temperature superpositioning. This is in accord with a recent study[20] of shear relaxation in both $Sn(PO_3)_2$ and $AgPO_3$ where the authors noted the presence of TRS for the divalent melt but clear breakdown in TRS for the monovalent $AgPO_3$. For $AgPO_3$ the study observed frequency dependent shear data collapse somewhat at both high and low temperatures but exhibited a dramatic shift in spectra occurring between 210 and 220 C that defied any collapse. This is precisely the range of temperatures where our decrease in $\beta(\tau)$ occurs and we suspect the transition in β we see in Fig. 3 is likely the source for the deviation from scaling seen for $AgPO_3$ in the shear relaxation study. The transition could also be seen as evidence for the existence of new modes of relaxation that can be accessed at higher temperatures[20], but this fails to explain why the transition is not present in any of the divalent melts. For example, both $LiPO_3$ and $Ba(PO_3)_2$ share a nearly equal β_{AVG} = 0.51 but while the β of $LiPO_3$ decreases at higher temperatures, that of $Ba(PO_3)_2$ remains largely unchanged. One possibility might lie in fundamental differences in how monovalent and divalent cations ~~can~~ coordinate with the nonbridging oxygens on PO_4 units. For divalent cations studied here, the coordination number (CN) ranges[21] between about 7 to 9 while for Na and Li it is only 5 and for Ag is less than 3. These changes indicate further weakening of the crosslinking in addition to the decreasing field strength and, in the case of $AgPO_3$, suggest that the Ag ion might be often coordinated to a *single* PO_4 unit, thus establishing local charge neutrality while not forming a crosslink with any neighboring PO_4 units. This situation is unique to the monovalent cation and is effectively what transpires in metaphosphoric acid, HPO_3, which Eisenberg[19] described as a "nonionic" polymer with zero field strength that exhibits an ultralow T_g = -10 C. We speculate that the $\beta(\tau)$ transition in the monovalent case might indicate a similar preference at higher temperatures for the cation to coordinate with NBOs on the same PO_4 unit.

5. Conclusions

Key to successful modeling of glass forming properties is a clearer understanding of the role of ionic bonding by modifying cations in contributing to the bond density of the network or to constraint-counting algorithms. The emerging picture suggests that such ionic bonds are more likely to participate in the network structure if the electrostatic field strength of cation-oxygen bond is high. Higher field strength promotes a stronger crosslinking between adjacent chains which stiffens the polymer structure and modifies the topology of the oxide structure from polymeric to continuous 3d network. Here we see how this modification leads to a decrease in the non-exponentiality consistent with a narrowing of the distribution of relaxation times.

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Figures

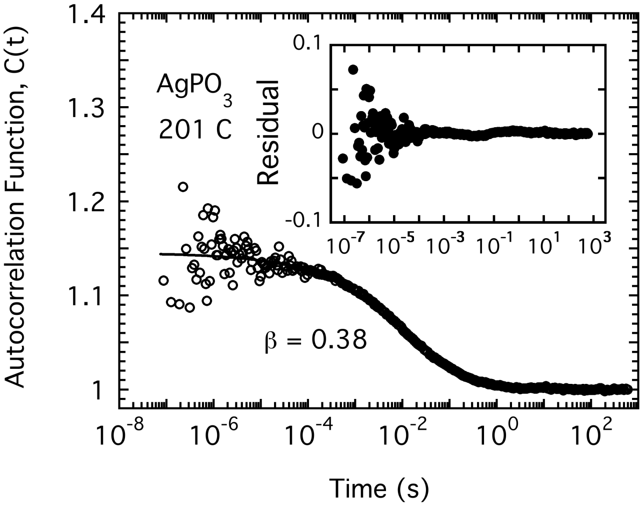

Fig. 1 Intensity autocorrelation function obtained from light scattered by $AgPO_3$ melt at 201 C. The decay is well fit by the stretched exponential function with β = 0.38. Inset: curve fit residuals show the stretched exponential provides a quality fit over some eight decades in time.

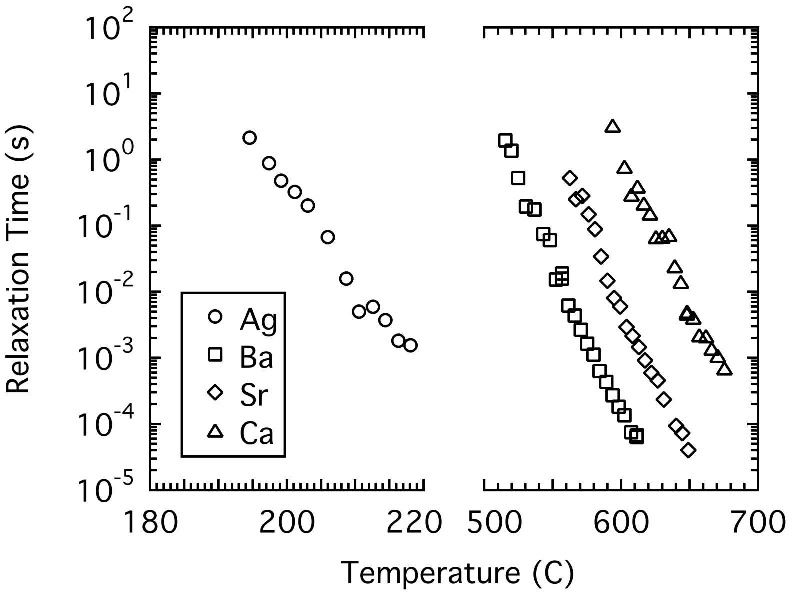

Fig. 2 Plot of the relaxation time for metaphosphate melts studied presently as a function of the temperature.

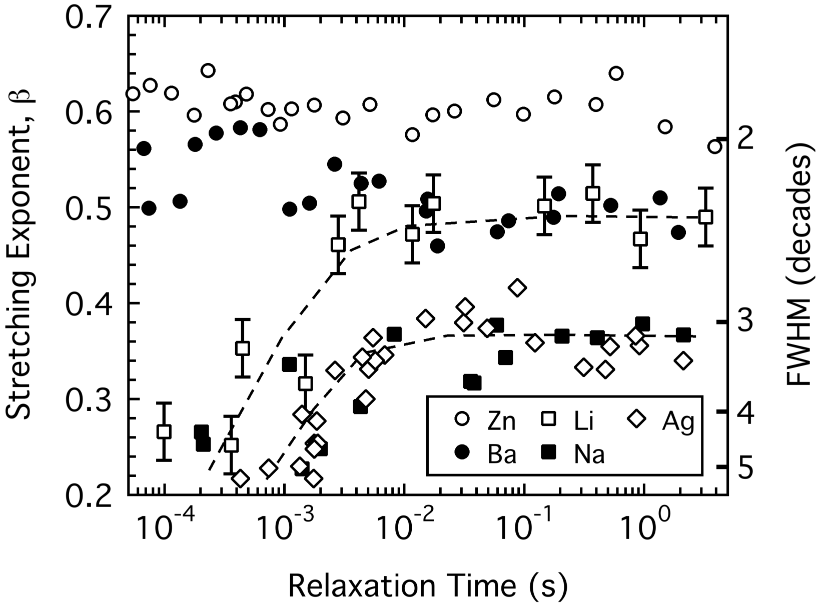

Fig. 3 The stretching exponent plotted against the relaxation time for a selection of metaphosphate glass melts. Near T_g, all exhibit a temperature-independent value β_{AVG}. In the case of monovalent cations, the β decreases as the relaxation time decreases below 10 milliseconds (dashed curves are guides only).

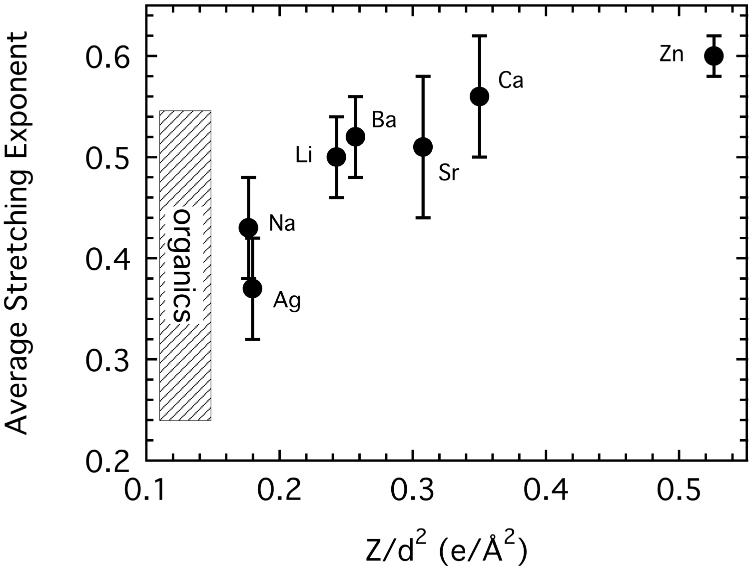

Fig. 4 Plot of the average β near T_g as a function of the modifying cation field strength. This parameter decreases with decreasing strength and approaches values similar to those reported in some conventional (non-ionic) polymers.