

Analysis of the Glass Transition Behavior of Polymer–Salt Complexes: An Extended Configurational Entropy Model

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A new molecular thermodynamic model is developed of the glass transition temperatures (T_g) of binary polymer–salt complexes by combining configurational entropy theory with Guggenheim's form of the Debye–Hückel theory. The interactions between the polymer chains and the salt as well as those between cations and anions are accounted for by this model. The predictions of this extended configurational entropy theory are compared with the T_g values of poly(2-ethyl-2-oxazoline) (POZ) complexed with AgBF_4 , AgClO_4 , AgCF_3SO_3 , and AgNO_3 at various compositions, as obtained by differential scanning calorimetry (DSC). The model accurately predicts the experimental T_g values even at high concentrations of silver salt (i.e., up to a mole ratio of $[\text{Ag}]/[\text{C}=\text{O}] = 1/1$), where the deviation of the simple configurational entropy theory from experimental data is large. Moreover, the maximum in the glass transition temperature, i.e., the increase in T_g with salt concentration at low salt concentrations but its decrease at high salt concentrations, is explicable with this model.

Introduction

Recently, there have been a large number of basic studies of ionic complexes made up of a polar polymer matrix and low lattice energy metal salts. Most investigations have been carried out on Li-based polyether complexes, because of their possible applications in a broad range of electrochemical devices.^{1–5} In studies of polymer electrolytes, the variation of the glass transition temperature (T_g) with metal salt concentration is of special interest.^{6–11} The dissolution of metal salts into the polymer matrixes not only generates charge carrier ions but also increases the rigidity of the polymer chains up to a moderately high salt concentration, resulting in a higher T_g . Because these two competing factors each have an opposite bearing on ion transport, the number of research efforts attempting to understand this glass transition behavior has been on the increase.

Polymer–metal complexes containing silver salts (i.e., silver polymer electrolytes) have been investigated for their use as facilitated olefin transport membranes for the separation of olefin/paraffin gas mixture.^{12–21} Their facilitated olefin transport is based on the reversible and specific complex-forming reactions between olefin molecules and silver ions dissolved in the polymer matrixes.^{22,23} The incorporation of silver salts into a polymer matrix causes the polymer chains to become more rigid because of transient cross-links between the chains and/or the dangling of metal atoms from the chains, resulting in an increased T_g and a consequent reduction in propane permeance.¹⁸ Therefore, variation in T_g depends largely upon the polymer electrolytes' structure, which in turn affects transport properties such as ionic conductivity and gas permeability.

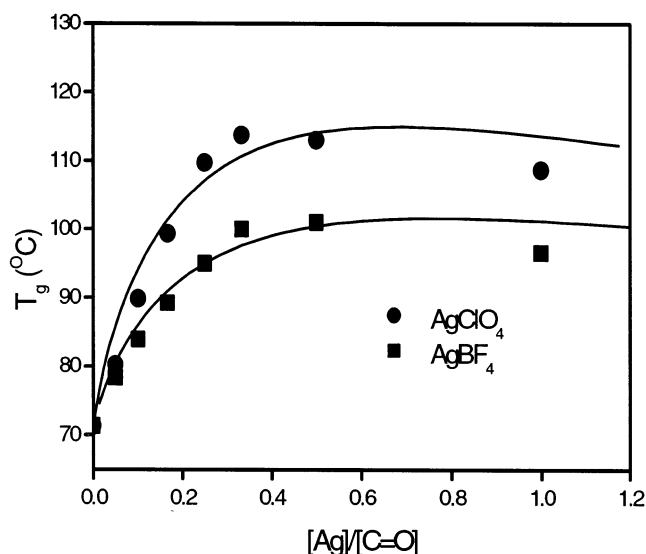


Figure 1. Glass transition temperatures with increasing salt concentration for POZ complexes with AgClO_4 and AgBF_4 .¹⁸ The solid lines are calculated with the simple configurational entropy model eq 6.

It has been frequently observed that in polymer electrolytes T_g increases with the metal salt concentration at low metal salt concentrations and reaches a broad maximum, followed by a decrease in T_g at high metal salt concentrations, as shown in Figure 1.¹⁸ The value of T_g in these polymer electrolytes provides information about the ionic interactions between the polymer matrix and the metal salts.^{24–26} It is well-known that the presence of metal salts leads to the loss of chain mobility and, as a consequence, to higher values of T_g . This increase in T_g is considered to be mostly associated with the polymer–cation and cation–anion interactions, because the polymer–

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anion interaction is thought not to be significant in common polymer electrolytes. This is especially true in silver polymer electrolytes, in which the cation–anion interaction is of pivotal importance in determining transport properties because it directly affects the complexation of olefin molecules with silver ions.^{17,24} For example, poly(2-ethyl-2-oxazoline) (POZ):AgBF₄ or poly(*N*-vinylpyrrolidone) (PVP):AgBF₄ electrolytes containing amide groups, with their rather strong silver cation–carbonyl oxygen and weak silver cation–anion interactions, exhibit favorable silver cation complexation with propylene molecules, resulting in high propylene solubility.¹⁷ These results suggest that the cation–anion interaction is important and needs to be considered along with the polymer–cation interaction if the structure and physical properties of polymer electrolytes are to be understood.

To our knowledge, there have been no previous studies of the influence of the cation–anion interaction on the variation of T_g in polymer electrolytes. The present research sets out to develop a molecular thermodynamic model of T_g in binary polymer–salt complexes by describing the ionic interaction between the metal cation and its counteranion using configurational entropy theory and the Debye–Hückel theory modified by Guggenheim.^{27,28} In addition, the maximum in the glass transition temperature of polymer–salt complexes, i.e., the increase in T_g with salt concentration at low salt concentrations but its decrease at high salt concentrations, can be interpreted with this new model.

Model Development

In developing our mathematical model, we followed earlier work,²⁵ and have added an account of the interactions between cations and anions. DiMarzio and Gibbs suggested that glass formation is a result of the system's loss of configurational entropy (S_c).^{29,30}

$$S_c = S^{\text{liquid}} - S^{\text{glass}} \quad (1)$$

where S^{liquid} and S^{glass} indicate the configurational entropies of the liquid and glass states, respectively.

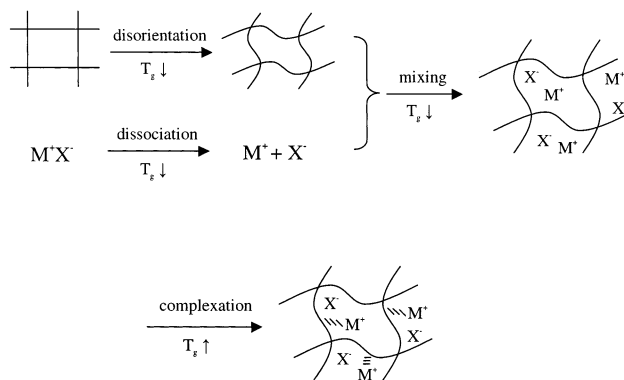
Following Chow's assumption³¹ that $S^{\text{glass}}(n_1, 0, T) = S^{\text{glass}}(n_1, n_2, T) = 0$ and that ΔC_p is independent of temperature and composition, the change in the glass transition temperature produced by addition of a second component such as a metal salt into the polymer matrix can be described by

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = -\frac{1}{\Delta C_p} [S_c(n_1, n_2, T) - S_c(n_1, 0, T)] \quad (2)$$

where T_{g1} and T_{g12} are the T_g of the pure polymer and of the polymer–salt complex, respectively, and ΔC_p is the difference in the heat capacity between the supercooled liquid and the glass. n_1 and n_2 are the numbers of molecules of components 1 (polymer) and 2 (salt), respectively.

In previous treatments of binary polymer–salt systems,²⁵ only three kinds of configurational entropy have been taken into account: the disorientation entropy of the polymer ($S_{\text{diso-1}}$) and the mixing ($S_{\text{mix-12}}$) and complexation entropies ($S_{\text{com-12}}$) for interactions between the polymer chains and the salt. Such treatments neglect the entropy associated with the interactions between cations and anions. The complexation entropy ($S_{\text{com-12}}$) is assumed to be proportional to the product of $S_{\text{diso-1}}$ and $S_{\text{mix-12}}$, because it is expected that the more active the disorientation of polymer segments and their mixing with the

SCHEME 1



salt, the higher the possibility of complexation.

$$S_{\text{diso-1}} = k_B n_1 \left[\ln r_1 + (r_1 - 1) \ln \left(\frac{z-1}{e} \right) \right] \quad (3)$$

$$S_{\text{mix-12}} = -k_B [n_1 \ln \phi_1 + n_2 \ln \phi_2] \quad (4)$$

$$S_{\text{com-12}} = k_B \gamma_{\text{com}} \ln \left(\frac{z-1}{e} \right) [n_1 \ln \phi_1 + n_2 \ln \phi_2] \quad (5)$$

where k_B is the Boltzmann constant. $\phi_1 = r_1 n_1 / (r_1 n_1 + r_2 n_2)$ and $\phi_2 = r_2 n_2 / (r_1 n_1 + r_2 n_2)$ are the volume fractions of components 1 and 2, respectively. $r_1 = v_1/v_0$ and $r_2 = v_2/v_0$, where v_1 and v_2 are the molar volumes of components 1 and 2, respectively, and v_0 is the unit lattice volume. For the polymer–salt system, we normally set $v_1 = v_0$ for convenience. Then $r_1 = 1$ and $r_2 = v_2/v_1$. z is the lattice coordination number. γ_{com} is a proportionality constant representing the complexation interaction between polymer and salt.

Equations 2–5 can be combined to provide a configurational entropy theory for the glass transitions of binary and ternary systems.²⁵

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = \beta \left[1 - \gamma_{\text{com}} \ln \left(\frac{z-1}{e} \right) \right] \left[\frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right] \quad (6)$$

where $\beta = zR/M_{1u}\Delta C_{pp}$. R , M_{1u} , and ΔC_{pp} are the gas constant, the molecular weight of the repeat unit and the isobaric specific heat jump of the polymer, respectively.

The solid lines in Figure 1 are the theoretical predictions of eq 6 for POZ complexes with AgBF₄ and AgClO₄. The simple configurational entropy theory of eq 6 predicts experimental glass transition temperatures very accurately up to $[\text{Ag}]/[\text{C}=\text{O}] = 0.5$; however, beyond this point these predictions start to deviate from experiment. In developing eq 6,²⁵ only polymer–salt interactions were considered, but the cation–anion interaction that is significant at high concentrations of silver salts was not. In this study, the configurational entropy theory is extended to account for the cation–anion interaction. The cation–anion interaction is treated here by including the dissociation entropy ($S_{\text{diss-2}}$), as given by the extended Debye–Hückel theory modified by Guggenheim.^{27,28} The complexation process of metal salts with polymers is drawn schematically in Scheme 1. From this scheme, S_c for binary polymer–salt systems can be described as follows.

$$S_c(n_1, n_2, T) = S_{\text{diso-1}} + S_{\text{diss-2}} + S_{\text{mix-12}} + S_{\text{com-12}} \quad (7)$$

$$S_c(n_1, 0, T) = S_{\text{diso-1}} \quad (8)$$

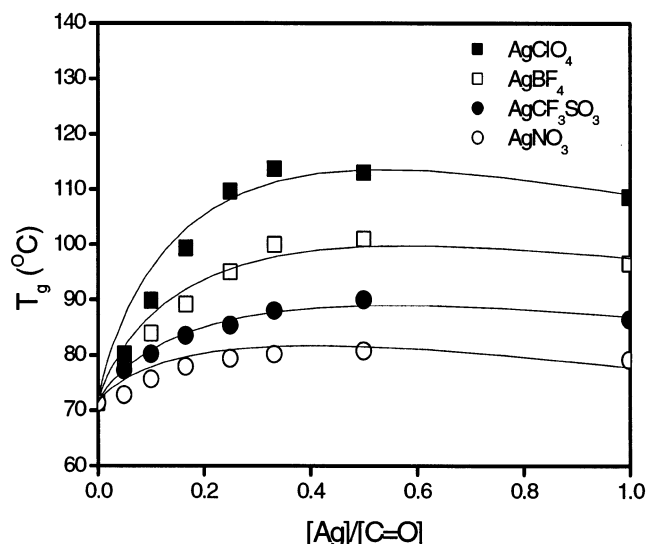


Figure 2. T_g variation of POZ complexes with silver salts. The solid lines are calculated with the extended configurational entropy model eq 11.

Substitution of eqs 7 and 8 into eq 2 yields

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = -\frac{1}{\Delta C_p} [S_{\text{diss}-2} + S_{\text{mix}-12} + S_{\text{com}-12}] \quad (9)$$

$S_{\text{diss}-2}$ is expressed as follows.^{27,28,32}

$$S_{\text{diss}-1} = \frac{k_B n_2}{mv} \left[\frac{4}{3} A_{\text{diss}} I^{3/2} \tau(I^{1/2}) \right] \quad (10)$$

Here, $\tau(x) = 3/x^3 [\ln(1+x) - x + x^2/2]$ and $I = 1/2 mv |z_M z_X|$, where m is a solute molality (mol/kg polymer). $\nu = \nu_M + \nu_X$; ν_M and ν_X are the number of M and X ions, respectively) is the number of ions per salt, A_{diss} is the Debye–Hückel coefficient, I is the ionic strength, M is the molecular weight of polymer in g/mol, and z_M and z_X are the valences of the M and X ions, respectively.

Substitution of eqs 4, 5, and 10 into eq 9 leads to the following extended configurational entropy model equation for the glass transition temperatures of binary polymer–salt systems.

$$\ln \frac{T_{g12}}{T_{g1}} = \beta \left[\left(1 - \gamma_{\text{com}} \ln \left(\frac{z-1}{e} \right) \right) \left(\frac{\phi_1}{r_1} \ln \phi_1 + \frac{\phi_2}{r_2} \ln \phi_2 \right) - \frac{\phi_2}{r_2 v m} \frac{4}{3} A_{\text{diss}} I^{3/2} \tau(I^{1/2}) \right] \quad (11)$$

Results and Discussion

Figure 2 presents the T_g variation of POZ:Ag salt complexes as a function of silver salt concentration. The dots and solid lines represent the experimental data from DSC and the curves calculated with eq 11, respectively. The glass transition temperatures of the POZ:Ag salt complexes increase gradually with silver salt concentration and then level off to reach a broad maximum, followed by decreases at high silver salt concentrations; this behavior is frequently observed in polymer electrolytes.^{7,8,25,26}

The T_g values predicted by the extended model are in excellent accord with the experimental values. Note that the agreement between the experimental and theoretical results is very good even at high silver salt concentrations, where the cation–anion interaction is strong enough to produce ion pairs,¹⁹

TABLE 1: Interaction Parameters of Polymer–Salt (γ_{com}) and Cation–Anion (A_{diss}) for POZ:Silver Salt Complexes

system	AgClO ₄	AgBF ₄	AgCF ₃ SO ₃	AgNO ₃
γ_{com}	1.100	0.978	0.920	0.866
A_{diss}	0.156	0.103	0.212	0.272

and that the simple configurational entropy theory of eq 6 starts to deviate from the experimental data at these concentrations, as shown in Figure 1. The model parameters γ_{com} and A_{diss} of eq 11 were obtained by nonlinear regression. γ_{com} represents the strength of the complexation interaction between the carbonyl oxygen of the polymer and the silver salt;²⁵ the higher the γ_{com} value, the stronger the interaction between polymer and salt. The extended model for T_g encompasses not only the complexation interaction between the polymer chains and the salt but also the ionic interactions between cations and anions. The value of A_{diss} in eq 11 represents the strength of the interaction between cation and anion.^{27,28} A small value of A_{diss} indicates a weak interaction between cation and anion, and vice versa. The polymer–salt interaction parameters (γ_{com}) and the cation–anion interaction parameters (A_{diss}) obtained for POZ:silver salt complexes are summarized in Table 1.

The strength of the polymer–salt interaction strongly depends on the counteranion and is ordered as follows: AgClO₄ > AgBF₄ > AgCF₃SO₃ > AgNO₃. On the other hand, the strength of the cation–anion interaction exhibits the following order: AgNO₃ > AgCF₃SO₃ > AgClO₄ > AgBF₄. As these sequences of the polymer–salt and cation–anion interaction strengths show, the two interactions are significantly correlated. For example, a polymer electrolyte with a strong cation–anion interaction such as POZ:AgNO₃ exhibits a relatively weak polymer–salt interaction and vice versa. The ionic interactions in POZ:Ag salt complexes have also been investigated previously by experimental spectroscopy as well as by theoretical ab initio calculation.¹⁷ It was found that (1) the strength of the cation–anion interaction has the order AgNO₃ > AgCF₃SO₃ > AgBF₄, and (2) the polymer–cation interaction exhibits the reverse order in strength, which agrees with the results derived from our extended configurational entropy theory. We conclude that the extended configurational entropy theory expressed by eq 11 yields a much better description of these polymer electrolyte systems than the simple configurational entropy theory expressed by eq 6. This is presumably due to the inclusion of cation–anion interactions in the extended model.

Although maxima in the glass transition temperatures of polymer electrolytes have been frequently observed experimentally, the understanding of this phenomenon is rather poor. The initial increase in T_g with increasing silver salt concentration can be interpreted as due to the resulting enhancement of the interaction between polymer chains and the silver salt. This enhanced interaction arises from the constraint of the polymer segments adjacent to silver ions by the transient cross-links created by coordination of silver ions with polymer chains and/or by the heavy ions dangling from polymer chains. If the only important interactions were those between the polymer chains and silver ions, T_g would be expected to increase monotonically with silver salt concentration. However, this is not the case, and therefore other factors should be considered.

The glass transition temperature reflects the rigidity of the polymeric chain segments. In polymer electrolytes, this rigidity, which is commonly characterized by the intersegmental distance, may depend strongly on the strength of the interaction between the polymer backbone and the metal salts. The intersegmental distances, d spacings, of POZ:silver salt complexes have been measured as a function of silver salt concentration by wide-

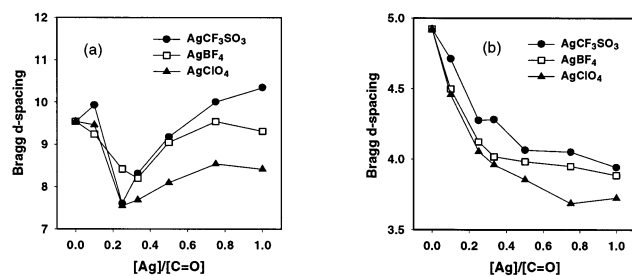


Figure 3. Bragg d spacings calculated from the positions of both peaks in POZ:Ag salt complexes with various silver concentration: (a) first peak; (b) second peak.¹⁸

angle X-ray scattering (WAXS)¹⁸ and are shown in Figure 3. At low silver salt concentrations, the d spacing decreases with increasing concentration, and increases for concentrations above approximately $[Ag]/[C=O] = 1/3$. It was suggested that the initial decrease is due to the interaction between polymer chains and salt whereas the increase is due to the repulsion between free anions. In other words, the slight decrease can be comprehended in terms of the enhancement of chain mobility at silver concentrations above $[Ag]/[C=O] = 1/3$ because of the increased interchain distance due to repulsion between anions. As a result, the glass transition temperatures for the POZ:Ag salt complexes increase at low salt concentrations and show broad maxima at around $[Ag]/[C=O] = 1/3$.

As described previously, the interaction between polymer and salt, which is particularly dependent on the type of ionic constituent that is present, plays an important role in determining the glass transition temperatures of polymer electrolytes. It has been found that three different ionic constituents are present, depending on the silver ion concentration: free ions, ion pairs, and higher order ion aggregates. The relative concentrations of each ionic constituent were measured for $AgCF_3SO_3$ dissolved in POZ or PVP by the use of Raman spectra in the region of the $\nu_s(SO_3^-)$ mode.^{16,19} After deconvoluting the $\nu_s(SO_3^-)$ stretching band into the bands due to free ions (1032 cm^{-1}), ion pairs (1038 cm^{-1}), and higher-order ionic aggregates (1048 cm^{-1}), the concentration of each constituent was calculated. As a result, it was found that only free ions are present up to $[Ag]/[C=O] = 1/2$, and that ion pairs start to form at around $[Ag]/[C=O] = 1/1$, followed by higher-order ionic aggregates at $[Ag]/[C=O] = 2/1$. Interestingly, free ions are not observable at $[Ag]/[C=O] = 3/1$. When silver ions are present as free ions, they can act as transient cross-linkers between polymer chains, resulting in an increase in T_g . However, once ion pairs or higher-order ionic aggregates start to form at high concentrations of the salt, silver ions may no longer act as transient cross-linkers and the interaction between polymer chains and salt may be weakened. The presence of ionic aggregates produces much weakened interactions between the polymer matrix and the silver salts, possibly resulting in a microphase separation of the polymer and salt phases. Thus the glass transition temperatures of polymer-salt complexes decrease gradually at high salt concentrations, possibly to values near T_g of the pure polymer. This analysis suggests that the decrease in T_g at high silver concentrations arises from the increased d spacing due to the electrostatic repulsion between anions, and from the decreased interaction between polymer chains and salts owing to the formation of ion pairs and/or higher order ion aggregates.

According to the configurational entropy model, as expressed by eq 9, variation in the glass transition temperature is a result of changes in the configurational entropy. The increase or decrease in T_g depends on whether the total entropy $S_{\text{total}} = S_{\text{diss-2}} + S_{\text{mix-12}} + S_{\text{com-12}}$ is above or below zero. T_g increases

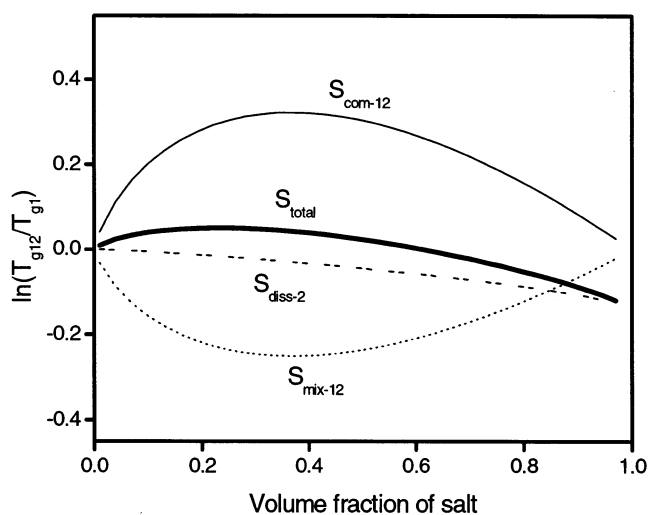


Figure 4. Dependence of T_{g12} on each entropy term as a function of volume fraction of salt. $S_{\text{com-12}}$, $S_{\text{diss-2}}$, and $S_{\text{mix-12}}$ represent the complexation, dissociation and mixing entropies, respectively. $S_{\text{total}} = S_{\text{diss-2}} + S_{\text{mix-12}} + S_{\text{com-12}}$.

when $S_{\text{total}} < 0$ whereas it decreases when $S_{\text{total}} > 0$. The contribution of each entropy term in eq 9 to the T_g variation was calculated for varying concentrations of salt; these results are presented in Figure 4. To simplify the system, the model parameters were assumed to have the following values: $r_1 = 7168$, $r_2 = 1$, $z = 12$, $\gamma_{\text{com}} = 0.92$, $A_{\text{diss}} = 0.212$, and $\beta = 0.68$. As can be seen from Figure 4, the values of $S_{\text{diss-2}}$ and $S_{\text{mix-12}}$ always lead to a decrease in the value of T_g in the complexes compared to the pure polymer. The T_g value by $S_{\text{diss-2}}$ continuously decreases with increasing salt concentration, whereas the T_g value by $S_{\text{mix-12}}$ shows a minimum because of the maximum popularity at a middle concentration. In contrast, the complexation entropy represented by $S_{\text{com-12}}$ always helps to reduce the randomness of the system, resulting in an increase in T_g . In particular, the T_g value by $S_{\text{com-12}}$ shows a maximum owing to the increased randomness in the middle range of the salt concentration. Therefore, the glass transition temperatures of polymer electrolytes exhibit a maximum with respect to salt concentration as long as $-S_{\text{com-12}} > S_{\text{diss-2}} + S_{\text{mix-12}}$ regardless of the structural changes and of the type of ionic constituent present. In this case, the overall T_g behavior depends primarily on the strength of the interactions between polymer chains and the salt.

Conclusions

An extended configurational entropy theory that includes Guggenheim's form of the Debye-Hückel theory to account for cation-anion interactions predicts the experimental T_g values of POZ:Ag salt complexes very accurately even at high salt concentrations. Furthermore, the strengths of the cation-anion interactions derived from application of the new model are in good agreement with previous results from vibrational spectroscopy and ab initio calculation. The maximum behavior of T_g in polymer electrolytes may be always observed as long as $-S_{\text{com-12}} > S_{\text{diss-2}} + S_{\text{mix-12}}$ because of the maximum behavior in entropy at a middle concentration. Such maxima will be more pronounced when the d spacing is increased because of electrostatic repulsion between anions and when the cation-anion interaction becomes strong enough to produce ion pairs and/or ion aggregates at high metal salt concentrations.

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