Molecular Model and Analysis of Glass Transition Temperatures for Polymer−Diluent−Salt Systems

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ABSTRACT: Three explicit mathematical models have been developed to predict glass transition temperatures of binary polymer−diluent and polymer−salt systems as well as ternary polymer−diluent−salt systems based on the configurational entropy model and the Flory−Huggins theory. In the presence of salt, the specific ionic interactions of polymer and/or diluent with salts have been taken into account. The validity of the mathematical models were examined against the experimental glass transition temperatures of poly(2-ethyl-2-oxazoline)−propylene carbonate, poly(2-ethyl-2-oxazoline)−silver triflate, and poly(propylene oxide)−lithium iodide as well as poly(2-ethyl-2-oxazoline)−propylene carbonate−silver triflate. The models adequately predict glass transition temperatures depending on the concentrations of the diluent as well as the salt in both binary and ternary systems.

Introduction

Polymer electrolytes are composed of low lattice energy salts dissolved in polymers containing polar groups such as oxygen, nitrogen, and sulfur. They generally form complexes via coordination bonds between metal ions and electron donor groups of polymer, which result from the competition between the solvation energy and the lattice energy of salt. The main body of researches about solid polymer electrolytes has been focused on the improvement in ionic conductivity (10^{-4} S/cm or better at room temperature) as well as in chemical, electrochemical, and mechanical stability. Ionic conductivity is a product of the carrier concentration and the carrier mobility. The carrier mobility is strongly associated with the chain mobility of a polymer medium, which is commonly measured by the glass transition temperature; i.e., the lower the glass transition temperature, the higher is the chain mobility. In this respect, a plasticizer has been commonly introduced to decrease the glass transition temperature and consequently to enhance the chain mobility and the ionic conductivity.[1,2] Therefore, prediction or estimation of the glass transition temperature in polymer electrolytes is important to understand their conduction behavior.

Di Marzio and Gibbs[3] argued that the true transitions could possess equilibrium properties even though the observed glass transitions were indeed a kinetic phenomenon. At infinitely long times, they predicted a true glass transition when the material finally reaches equilibrium and when the entropy becomes zero. From the configurational partition function of the quasi-lattices, Adam and Gibbs[4] have developed a lattice model that predicts the equilibrium glass transition (T_2) and the glass transition depression by plasticizer. Chow[5] has extended the Di Marzio−Gibbs work[3] by deriving an explicit expression for T_g of polymer−diluent systems. In this treatment the effect of polymeric chain length is not considered because his model is based on the simple Bragg−William theory.[6] Thus, a mixing entropy is overestimated, and a lattice coordination number ($z = 2$) is underestimated. Sanchez and coworkers[7−10] also proposed a refined lattice model using the lattice fluid theory as well as the Di Marzio−Gibbs criterion.[3] Here four fundamental types of T_g vs pressure behavior were identified and *retrograde vitrification* was predicted.[7] Couchman and Karasz[11] treated the glass transition as a second-order transition and used the characteristic continuity and discontinuity conditions of such phenomena to describe the effect of composition on T_g for a binary system. Di Marzio et al.[12] predicted, to a good approximation, the glass temperature depression as a nearly universal function of total mole fraction of diluent. More recently, Dong and Fried[13] reported a different lattice model for the glass transition of both pure and plasticized polymers including gas−polymer systems. In their model, the criterion for glass transition is taken to be the vanishing of the entropy pertaining to the nonlocal movements of polymer segments rather than the total mixing entropy of the system.

In this study, we proposed simple, molecular−thermodynamic models for binary polymer−diluent and polymer−salt systems as well as for ternary polymer−diluent−salt systems. These models have been developed by extending the Chow model[5] for T_g of binary polymer−diluent systems and the Flory−Huggins lattice theory.[14] The validity of the models were examined against experimental glass transition temperatures for polymer electrolytes of binary poly(2-ethyl-2-oxazoline)−$AgCF_3SO_3$ and poly(propylene oxide)−LiI,[15] and ternary poly(2-ethyl-2-oxazoline)−propylene carbonate−$AgCF_3SO_3$.

Model Development

The glass formation is considered as a result of the system's loss of configurational entropy (S_c) from the viewpoint of Di Marzio−Gibbs[3]

$$S_c = S^{\text{liquid}} - S^{\text{glass}} \tag{1}$$

where S^{liquid} and S^{glass} represent the configurational entropy of the liquid state and of the glass state, respectively.

Binary Polymer−Diluent System. For a binary system of polymer (component 1) and diluent (component 2), the configurational entropy S_c is related by[3,5]

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$$S_c(n_1,n_2,T) = \int_{T_{g12}}^{T} \Delta C_p(n_1,n_2,T')\, d(\ln T') \qquad (2)$$

where n_1 and n_2 are the numbers of the molecules of components 1 and 2, respectively. ΔC_p is the difference in heat capacity between the supercooled liquid and the glass. T_{g12} is the glass transition temperature of the mixture of 1 and 2.

Following the assumptions of Di Marzio and Gibbs[3] and Chow,[5] we also set $S^{glass}(n_1,0,T) = S_{glass}(n_1,n_2,T) = 0$. The configurational entropy S_c is then equal to S^{liquid}. In addition, ΔC_p is assumed to be independent of temperature and composition as it was.[5] Equation 2 is, then, readily integrated, and the change in the glass transition temperature due to the addition of diluent (component 2) is written by the difference in the configurational entropy as

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = -\frac{1}{\Delta C_p}[S_c(n_1,n_2,T) - S_c(n_1,0,T)] \qquad (3)$$

where T_{g1} is the glass transition temperature of component 1.

Chow[5] followed the Bragg-William approach[6] to calculate the configurational entropy in eq 3. However, we instead used the Flory−Huggins theory[14] for more generalization, especially for considering a binary polymer−salt system with specific ionic interactions. The configurational entropy in the Flory−Huggins theory constitutes the disorientation, S_{dis-1}, and the mixing, S_{mix-12}, terms ($S_c = S_{dis-1} + S_{mix-12}$) and is given by[14]

$$S_c(n_1,n_2,T) = k_B\left[n_1\left[\ln r_1 + (r_1 - 1)\ln\left(\frac{z-1}{e}\right)\right] - [n_1 \ln \phi_1 + n_2 \ln \phi_2]\right] \qquad (4)$$

where k_B is the Boltzmann constant. z is the lattice coordination number. $\phi_1 = r_1n_1/(r_1n_1 + r_2n_2)$ and $\phi_2 = r_2n_2/(r_1n_1 + r_2n_2)$ 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 the components 1 and 2, respectively, and v_0 is the unit lattice volume. For polymer (1)−diluent (2) system, we normally set $v_2 = v_0$ for convenience. Then $r_1 = v_1/v_2$ and $r_2 = 1$.

Substitution of eq 4 into eq 3 leads to

$$\ln\frac{T_{g12}}{T_{g1}} = \beta_1\left[\frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_2}{r_2}\ln \phi_2\right] \qquad (5)$$

where $\beta_1 = (k_B\xi/\Delta C_p)$ where ξ is the total number of lattices and $\xi = (r_1n_1 + r_2n_2)$ for the binary system. We again followed the Chow assumptions of $\xi = z(m_1/M_{1u})N_A$ and $\Delta C_p = m_1\Delta C_{pp}$, where m_1, M_{1u}, and ΔC_{pp} are the weight, the molecular weight of the repeat unit, and the isobaric specific heat of the polymer, respectively. N_A is the Avogadro number. Thus, β_1 can be written again as

$$\beta_1 = \frac{zR}{M_{1u}\Delta C_{pp}} \qquad (6)$$

where R is the gas constant. Thus, β_1 depends only on the type of polymer.

Binary Polymer−Salt System. For the binary polymer (component 1)−salt (component 3) system, the salts will be dissolved in a polymer matrix. Therefore, the specific ionic interactions such as ion−polymer and ion−ion interactions should be additionally considered because such interactions reduce the overall entropy. In developing a mathematical model, the following assumptions are made: (1) salts are completely dissolved into cations and anions in the polymer matrix, and (2) the difference between the cation and the anion of salts has not been taken into account. Therefore, S_c for a binary polymer−salt system constitutes the ionic entropy term S_{ion-13} in addition to S_{dis-1} and S_{mix-13}: $S_c = S_{dis-1} + S_{mix-13} - S_{ion-13}$.

S_{ion-13} will be assumed to be proportional to a product of S_{mix-13} and S_{dis-1u} (disorientation of unit polymer), i.e., $S_{ion-13} = (\gamma_{ion-13}/k_B)S_{mix-13}S_{dis-1u}$ where γ_{ion-13} is a proportionality constant representing the ionic interaction between polymer and salt. This relation is based on the expectation that "the more active both the mixing and the disorientation of polymer segments, the higher the possibility of specific ionic interaction". Hence

$$S_c(n_1,n_3,T) = -k_B\left[(n_1 \ln \phi_1 + n_3 \ln \phi_3)\left(1 - \gamma_{ion-13} \times \ln\left(\frac{z-1}{e}\right)\right) - n_1\left(\ln r_1 + (r_1 - 1)\ln\left(\frac{z-1}{e}\right)\right)\right] \qquad (7)$$

where $\phi = r_1n_1/(r_1n_1 + r_3n_3)$ $\phi_3 = r_3n_3/(r_1n_1 + r_3n_3)$; $r_3 = 1$ for salt ion; n_3 is the number of ions.

Equation 3 modified for a polymer−salt system and eq 7 lead to

$$\ln\left(\frac{T_{g13}}{T_{g1}}\right) = \beta_1\left[\left(\frac{\phi_1}{r_1}\ln \phi_1 + \frac{\phi_3}{r_3}\ln \phi_3\right)\left(1 - \gamma_{ion-13} \times \ln\left(\frac{z-1}{e}\right)\right)\right] \qquad (8)$$

where T_{g13} is the glass transition temperature for the polymer−salt system. According to eq 8, the T_g elevation will be expected only if $S_{mix-13} - S_{ion-13} < 0$. If γ_{ion-13} is zero, eq 8 reduces to the same form as eq 5.

Ternary Polymer−Diluent−Salt System. For ternary polymer−diluent−salt systems, $S_c(n_1,n_2,n_3,T)$ constitutes two negative contribution terms due to the polymer-ion S_{ion-13} and diluent-ion S_{ion-23} interactions in addition to the disorientation S_{dis-1} and mixing $S_{mix-123}$ terms: $S_c = S_{dis-1} + S_{mix-123} - S_{ion-13} - S_{ion-23}$. When the diluent and the salt are low molecular additives, their disorientation effect is not taken into account. Hence

$$S_{ion-23} = -\gamma_{ion-23}k_B(n_2 \ln \phi_2 + n_3 \ln \phi_3) \qquad (9)$$

where γ_{ion-23} is a proportionality constant representing the ionic interaction between the diluent and salt.

In the case of the addition of a diluent into a binary polymer−salt system, the glass transition temperature T_{g123} of the ternary system is readily obtained:

$$\ln\left(\frac{T_{g123}}{T_{g13}}\right) = \beta_1\left[\left(\frac{\varphi_1}{r_1}\ln \varphi_1 + \frac{\varphi_2}{r_2}\ln \varphi_2 + \frac{\varphi_3}{r_3}\ln \varphi_3\right) - \left(\frac{\varphi_1}{r_1}\ln \phi_1 + \frac{\varphi_3}{r_3}\ln \phi_3\right) - \gamma_{ion-23}\left(\frac{\varphi_2}{r_2}\ln \phi_2 + \frac{\varphi_3}{r_3}\ln \phi_3\right)\right] \qquad (10)$$

where φ_i ($i = 1, 2, 3$) is the volume fraction of component i for the ternary system and ϕ_i ($i = 1, 2, 3$) is the volume fraction of component i for the binary system.

In the case of the introduction of salts in a polymer−diluent system, the T_{g123} will be expressed in terms of

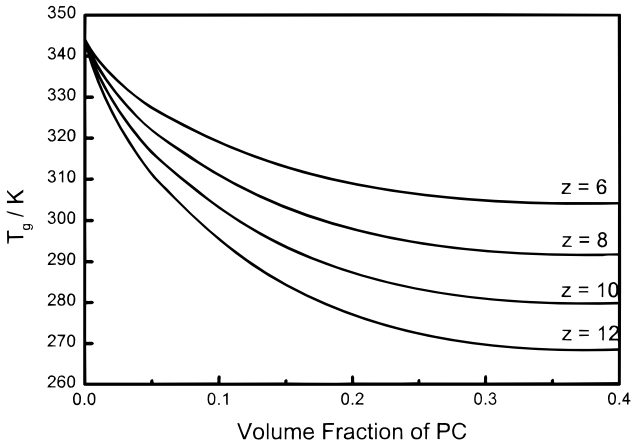

Figure 1. Theoretical predictions of T_g as a function of the volume fraction of diluent with varying lattice coordination number (z = 6, 8, 10 and 12) for the POZ−PC system. Solid lines are calculated from eq 5, where the physical parameters used are T_{g1} = 344 K, β_1 = 0.0567z, r_1 = 5113, and r_2 = 1.

T_{g12} as follows:

$$\ln\left(\frac{T_{g123}}{T_{g12}}\right) = \beta_1\left[\left(\frac{\varphi_1}{r_1}\ln\varphi_1 + \frac{\varphi_2}{r_2}\ln\varphi_2 + \frac{\varphi_3}{r_3}\ln\varphi_3\right) - \left(\frac{\varphi_1}{r_1}\ln\phi_1 + \frac{\varphi_2}{r_2}\ln\phi_2\right) - \gamma_{ion-13}\left(\frac{\varphi_1}{r_1}\ln\phi_1 + \frac{\varphi_3}{r_3}\ln\phi_3\right) \times \ln\left(\frac{z-1}{e}\right) - \gamma_{ion-23}\left(\frac{\varphi_2}{r_2}\ln\phi_2 + \frac{\varphi_3}{r_3}\ln\phi_3\right)\right] \quad (11)$$

From this model, we can predict T_g for the polymer−diluent−salt system with increasing the salt concentration.

Experimental Section

Sample Preparation. Poly(2-ethyl-2-oxazoline) (POZ) (M_w = 500 kg/mol), propylene carbonate (PC) (99%), and $AgCF_3SO_3$ (98%) were purchased from Aldrich Chemical Co. and were used without further purification. For the POZ−$AgCF_3SO_3$ and the POZ−PC−$AgCF_3SO_3$ systems, all the components were dissolved in distilled water and stirred for several hours at room temperature, and then cast on a precleaned Teflon plate. Films were dried for 24 h under N_2 environment and then transferred to a vacuum oven. They were dried under vacuum at room temperature for 72 h.

Differential Scanning Calorimetry. Perkin-Elmer DSC-7 was used to measure glass transition temperatures at a heating rate of 20 °C/min under nitrogen environment. The glass transition temperature was selected as the maximum temperature of the peak.

Results and Discussion

Binary Polymer−Diluent System. Figure 1 shows the theoretical predictions of T_g calculated from eq 5 as a function of the volume fraction of diluent with varying lattice coordination number (z) for the POZ−PC system. The physical parameters for theoretical calculations are summarized in Tables 1 and 2: T_{g1} = 344 K, β_1 = 0.0567z, r_1 = 5113, and r_2 = 1. As expected, Figure 1 demonstrates that the presence of low molecular weight compounds lowers the T_g values. Furthermore, the T_g value is depressed more effectively with increasing z values.

Binary Polymer−Salt System. The experimental glass transition temperatures of the POZ−$AgCF_3SO_3$ system were compared with theoretical predictions as shown in Figure 2. Open circles represent experimental glass transition data obtained from the DSC thermograms. The T_g value gradually increases with adding salts because of the increased ion−polymer and ion−ion interactions. When silver cations coordinate with the oxygen atoms of the carbonyl groups of POZ, their chain mobility will be reduced and consequently T_g will be increased. The reduced mobility may be due to the facts that (1) the coordination of metal ion is equivalent to the introduction of large bulky side groups and (2) the anions may act as ionic cross-links when the cations, in particular, strongly coordinate with functional groups of the polymer. The T_g value levels off at high salt concentrations, which has been commonly observed beyond the solubility limit of the salt in a polymer matrix.[18,19]

The solid line in Figure 2 is calculated from eq 8 with β_1 = 0.68, γ_{ion-13} = 0.86, and r_1 = 7168 as summarized in Tables 1 and 2, where the γ_{ion-13} value is obtained by nonlinear regression.[16] Flory[14] proposed that the "z" value should be from 6 to 12, and that the higher the "z" value is, the more realistic is the theoretical model. Therefore, we take it as 12 to calculate β_1. The agreement between theoretical predictions and experimental data was very good up to the weight fraction of the salt of 0.4. Beyond this concentration, the disparity increases, which may be due to the assumption of com-

Table 1. List of Molecular Weight, Glass Transition Temperature, Specific Heat, and Density of Components Used

	MW (kg/mol)	T_g (K)	ΔC_{pp}[a] (J/(kg K))	ρ (kg/m^3)
POZ	500	344	1480	1140
PPO	4	200	1930	1000
PC	0.102	192		1189
$AgCF_3SO_3$	0.257			4200[a]
LiI	0.134			3490

[a] Values obtained from the group contribution method.[17]

Table 2. Model Parameters To Calculate the Glass Transition Temperatures

system	z	β_1^{*a}	γ_{ion-13}	γ_{ion-23}
POZ/PC	12	0.68		
POZ/$AgCF_3SO_3$	12	0.68	0.86	
POZ/$AgCF_3SO_3$/PC	12	0.68	0.86	0.32
PPO/LiI	12	0.89	1.89	

[a] $\beta_1^* = zR/(M_{1u}\Delta C_{pp})$.

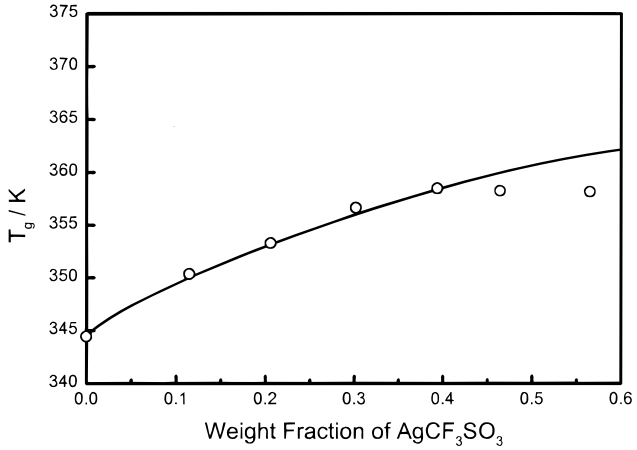

Figure 2. Comparison of the theoretical predictions with experimental glass transition temperatures for the POZ−$AgCF_3SO_3$ system. The solid line is calculated from eq 8, where T_{g1} = 344 K, β_1 = 0.68, r_1 = 7168, r_3 = 1, and γ_{ion-13} = 0.86.

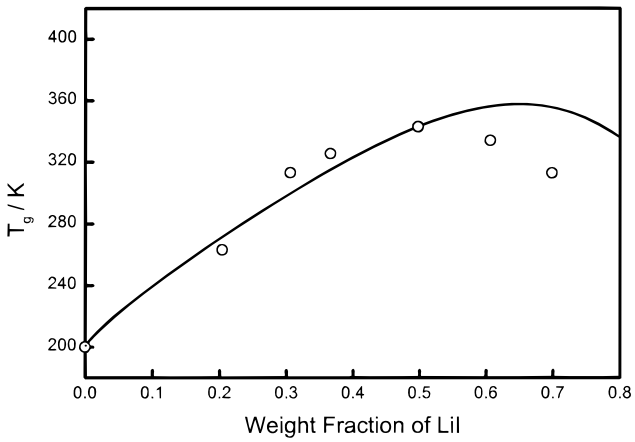

Figure 3. Comparison of the theoretical predictions with experimental glass transition temperatures for the PPO−LiI system. Open circles are experimental data by Angell et al.[15] The solid line is calculated form eq 8, where $T_{g1} = 200$ K, $\beta_1 = 0.89$, $r_1 = 70$, $r_3 = 1$, and $\gamma_{ion-13} = 1.89$.

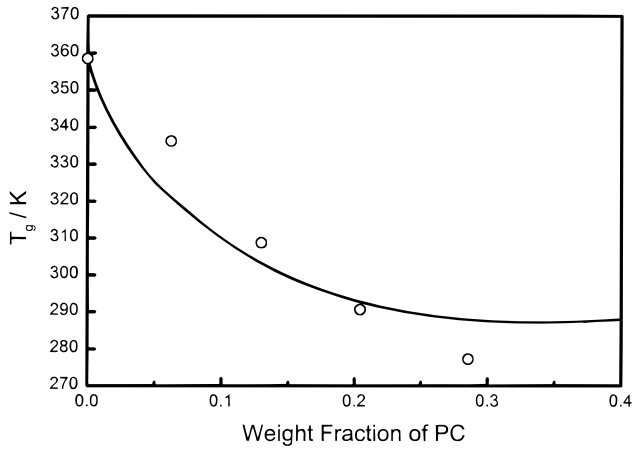

Figure 4. Comparison of the theoretical predictions with experimental glass transition temperatures for the POZ−PC−$AgCF_3SO_3$ system as a function of the PC concentration with the weight fraction of $AgCF_3SO_3$/(POZ + $AgCF_3SO_3$) fixed at 0.4. The solid line is calculated from eq 10, where $T_{g13} = 359$ K, $\beta_1 = 0.68$, $r_1 = 7168$, $r_2 = 1$, $r_3 = 1$, and $\gamma_{ion-23} = 0.32$.

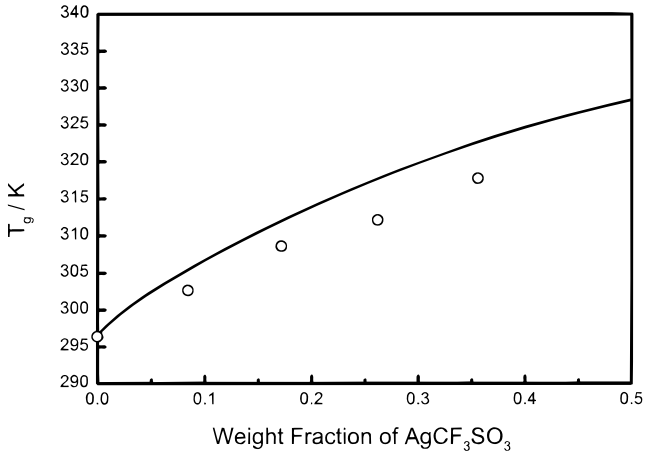

Figure 5. Comparison of the theoretical predictions with experimental glass transition temperatures for the POZ−PC−$AgCF_3SO_3$ system as a function of the $AgCF_3SO_3$ concentration with the weight fraction of PC/(POZ + PC) fixed at 0.17. The solid line is calculated from eq 11, where $T_{g12} = 296$ K, $\beta_1 = 0.68$, $r_1 = 7168$, $r_2 = 1$, $r_3 = 1$, $\gamma_{ion-13} = 0.86$, and $\gamma_{ion-23} = 0.32$.

plete dissolution of salts. This assumption may not be true at concentrations above the solubility limit of the salt, where the salts are present as ion pair or ion aggregates instead.[18,19]

Figure 3 shows the T_g behavior of the PPO−LiI system. The solid line is calculated from eq 8 with $\beta_1 = 0.89$, $\gamma_{ion-13} = 1.89$, and $r_1 = 70$. Open circles are experimental data by Angell et al.,[15] who thought that the maximum T_g value could serve to separate the "salt-in-polymer" and "polymer-in-salt" domains. On comparing the PPO−LiI system with the POZ−$AgCF_3SO_3$ system, the change in T_g is much higher in the PPO−LiI system than the POZ−$AgCF_3SO_3$ system, where the value for γ_{ion-13} of the former is 1.89 and that for the latter 0.86. This represents that the ionic interaction between polymer and salt is stronger in the PPO−LiI system than in the POZ−$AgCF_3SO_3$ system. It is worth noting that the T_g elevation in "salt-in−polymer" domains can occur, only when S_{ion-13} quantitatively exceeds S_{mix-13}. However, the T_g depression could occur only when S_{mix-13} is higher than S_{ion-13}.

Ternary Polymer−Diluent−Salt System. Figure 4 shows the T_g depression as a function of the PC concentration for the ternary POZ−PC−$AgCF_3SO_3$ system. Open circles are experimental glass transition temperatures with the weight fraction of $AgCF_3SO_3$/(POZ + $AgCF_3SO_3$) fixed at 0.4. The T_g value decreases sharply with the concentration of PC due to its plasticizing effect with relatively high dielectric constant, 64.4. The solid line in Figure 4 is calculated from eq 10 with $\beta_1 = 0.68$, $\gamma_{ion-23} = 0.32$ and $r_1 = 7168$. The higher value of γ_{ion-13} (0.86) compared with γ_{ion-23}(0.32) represents the point that the interaction of $AgCF_3SO_3$ with carbonyl groups of POZ is more favorable than that of PC.

When salts are added into polymer−diluent system, the glass transition temperature will increase. Figure 5 shows the T_g elevation as a function of the Ag salt concentration for the POZ−PC−$AgCF_3SO_3$ system with the weight fraction of [PC/(POZ + PC)] fixed at 0.17. Open circles are experimental data. The solid line is calculated from eq 11 with $\beta_1 = 0.68$, $\gamma_{ion-13} = 0.86$, $\gamma_{ion-23} = 0.32$, and $r_1 = 7168$, where the parameters values are not modified further. As shown in Figure 5, the agreement between the theoretical predictions (which is not data fitting) and the experimental data is fairly good, but the former slightly overestimates the latter.

Conclusion

Three explicit mathematical models were derived based on classical and statistical thermodynamics to predict the glass transition temperatures of both binary and ternary systems including salt. When salts are present, it was assumed that (1) the salts are completely dissolved into cations and anions in polymer matrix and that (2) the difference between cations and anions of the salts has not been taken into account. Further, the parameter γ_{ion} was introduced to account for the ionic interactions of polymer and/or diluent with salts. The theoretical predictions were examined against the experimental glass transition temperatures of the binary POZ−$AgCF_3SO_3$, the PPO−LiI systems and the ternary POZ−PC−$AgCF_3SO_3$. It is concluded that the current models adequately predict the T_g dependence on the concentrations of diluent and of salt in both binary and ternary systems as well as on their ionic interactions.

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