Viscosity and Fragility of Polymer Electrolytes based on PPO and PPG

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The Bond Strength-Coordination Number Fluctuation (BSCNF) model and the Williams-Landel-Ferry (WLF) equation have been used to study the temperature dependence of the viscosity of polymer electrolytes $NaCF_3SO_3$ - PPO (4000), $NaCF_3SO_3$ - PPG (4000) and $LiClO_4$ - PPG (4000). The result indicates that both models describe well the temperature dependence of the viscosity reported experimentally. The analysis based on the BSCNF model suggests that by increasing the salt content, the fragility index increases due to the decrease of the connectivity between the structural units. The result indicates also that the empirical parameters used in the WLF equation could be related with the parameters of the BSCNF model.

§1. Introduction

Studies of physical properties of ion conducting polymeric materials are interesting from both, the academic and applied science points of views. These materials are characterized by their high ionic conductivity and high energy density power. Potential applications of these materials in rechargeable lithium-ion batteries, fuel cells, electrochromic displays, sensor, etc. have been investigated intensively. Many studies have been also conducted in order to enhance the ionic conductivity and the mechanical stability of these materials. However, fundamental understanding on the physical properties of the materials is not sufficient.

Previous studies have indicated that the optimization of the ionic conductivity could be searched by studying the viscosity-conductivity relation.[1), 2)] Following these studies, in the present report, the temperature dependence of the viscosity of polymer electrolyte systems, $NaCF_3SO_3$ - PPO (4000), $NaCF_3SO_3$ - PPG (4000) and $LiClO_4$ - PPG (4000) are investigated by the Bond Strength-Coordination Number Fluctuation (BSCNF) model[3)] and the Williams-Landel-Ferry (WLF) equation.[4)]

The polymer electrolyte systems considered in this study have been investigated by many authors.[5), 6)] Therefore, they are convenient materials for our purposes, that is, to test the validity of our model. The experimental data of the viscosities of Poly(propylene oxide) (PPO) and Poly(propylene glycol) (PPG) with molecular weight 4000 liquid polymer electrolytes containing dissolved sodium triflate ($NaCF_3SO_3$) and lithium perchlorate ($LiClO_4$) at different concentrations were taken from the papers of McLin and Angell.[5), 6)]

§2. Models for Viscosity and Fragility

2.1. *The BSCNF Model*

In the BSCNF model, the melt is considered to be formed by an agglomeration of structural units. When the temperature of the system is lowered, the viscosity of the melt increases due to the increase of the connectivity between the structural units and the spatial distribution of the structural unit is frozen at the glass transition temperature T_g. According to the model, the viscous flow occurs when the structural units move from one position to another by breaking and twisting the bonds connecting them. According to this model, the temperature dependence of the viscosity is written as[3)]

$$\ln\left(\frac{\eta}{\eta_0}\right)=\frac{Cx+Cx^2\left\{\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right]\frac{(1-B)}{C}-1\right\}}{1-Bx^2}-\frac{1}{2}\ln\left(1-Bx^2\right), \tag{2.1}$$

where

$$B=\frac{(\Delta E)^2(\Delta Z)^2}{R^2T_g^2}, \qquad C=\frac{E_0Z_0}{RT_g}, \qquad \text{and} \qquad x=\frac{T_g}{T}. \tag{2.2}$$

Here η_0 and η_{Tg} are the viscosities at the high temperature limit and at the glass transition temperature, respectively. For these values, we adopt the usual values[7)] $\eta_0 = 10^{-5}$ Pa·s and $\eta_{Tg} = 10^{12}$ Pa·s. E_0 and Z_0 are the average values of the binding energy and coordination number of the structural units, respectively. ΔE and ΔZ are their fluctuations and R is the gas constant. Note that C contains information about the total bond strength of the structural unit and B gives its fluctuation.

According to the BSCNF model, the fragility index m is written in terms of the parameters B and C as[3), 8)]

$$m=\frac{B-C+2\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\ln(1-B)}{(\ln 10)(1-B)}. \tag{2.3}$$

From Eq. (2.3), we can learn that a high value of the total bond strength of the structural unit C and a low value of its fluctuation B corresponds to a less fragile system. [1)]

2.2. *The WLF Equation*

The WLF equation has been used widely to describe the temperature dependence of the viscosity and relaxation time in polymeric systems.[4)] It is an empirical equation and is given by

$$\log a_T = \log\left(\frac{\eta}{\eta_{Tg}}\right) = \frac{-C_1(T-T_g)}{C_2+(T-T_g)} \quad , \tag{2.4}$$

where a_T is called shift factor. η is the viscosity at temperature T and η_{Tg} is the viscosity at some reference temperature. In the present analysis, we have used the glass transition temperature T_g as the reference temperature. C_1 and C_2 are constants. It has been reported that the values of C_1 and C_2 are 17.4 and 51.6 K respectively, for many materials.[4), 9)] In terms of the WLF parameters, the fragility is given by

$$F = 1 - \frac{C_2}{T_g} \quad . \tag{2.5}$$

§3. Results and Discussion

We have applied the BSCNF model and the WLF equation to analyze the experimental data of polymer electrolyte systems, $NaCF_3SO_3$ - PPO (4000), $NaCF_3SO_3$ - PPG (4000) and $LiClO_4$ - PPG (4000). From the analysis we have determined the values of the parameters (B, C) and (C_1, C_2) corresponding to each models. They are summarized in Table 1. The analysis revealed that both models describe well the temperature dependence of the viscosity reported experimentally. Concerning the value of the fragility index m and F, they have been determined from Eqs. (2.3) and (2.5), respectively.

Table I. Numerical values of the parameters of BSCNF (B, C) and WLF (C_1, C_2) equations of polymer electrolytes systems A: $NaCF_3SO_3$ - PPO (4000), B: $NaCF_3SO_3$ - PPG (4000), and C: $LiClO_4$ - PPG (4000). The numbers within the parenthesis in the compound column indicate the molar ratio between salts and polymers.

Polymers	***B***	***C***	C_1	C_2**(K)**	***F***	***m***
A(1:8)	0.71	9.8	15.1	31.0	0.88	107
A(1:10)	0.70	10.2	15.5	34.3	0.86	102
A(1:16)	0.65	10.9	15.5	36.4	0.84	87
A(1:30)	0.62	11.2	15.8	38.3	0.82	77
B(1:8)	0.74	11.1	15.2	31.2	0.88	118
B(1:16)	0.69	13.0	15.3	34.0	0.85	95
B(1:40)	0.68	13.2	15.8	37.3	0.82	91
C(1:8)	0.66	10.5	15.8	43.1	0.84	89
C(1:16)	0.60	11.7	16	46.7	0.79	72
C(1:40)	0.59	11.8	16.2	44.0	0.78	70

The result reveals that the addition of salt content to the polymer systems, e.g. data points from A (1:30) to (1:8), increases the value of B and decreases the value of C. This trend is reflected in the increase of the fragility by adding salt.

Concerning the parameters of the WLF equation, from Table I we note that C_2 is more sensitive than C_1 to the composition. A comparison between C_2 and the fragility index m described by the BSCNF model is shown in Fig. 1. We note that m decreases with the increase of C_2. The result indicates that the parameter C_2 of the WLF equation can be described in terms of the parameters of the BSCNF model which have clear physical meaning as defined in Eq. (2.2). Fig. 2 shows a comparison between the fragility index described by the BSCNF model m and the values of fragility based on the WLF equation F. It is recognized that there is a good correlation between these two set of values.

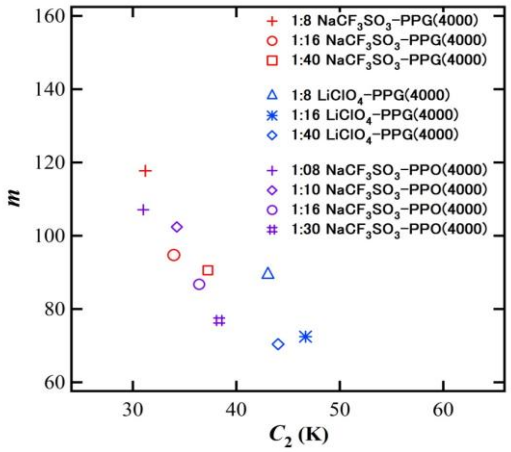

Fig. 1. Relationship between the fragility calculated from the BSCNF model, Eq. (2.3) and the value of the parameter C_2 in the WLF equation.

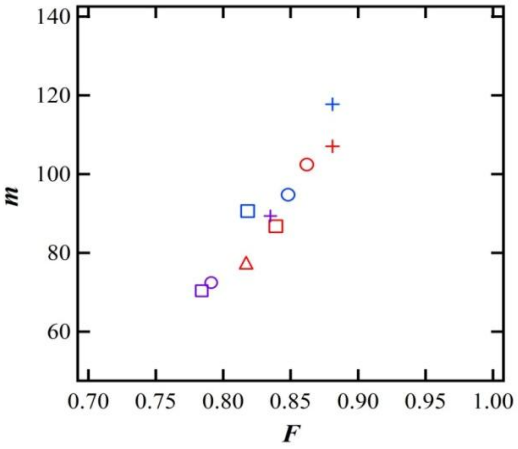

Fig. 2. Relationship between the fragility calculated from the BSCNF model, Eq. (2.3) and the fragility given by Eq. (2.5).

The temperature dependence of the viscosity calculated through Eq. (2.1) is shown in Fig. 3. We can note that the system in consideration is relatively fragile. According to the BSCNF model, the increase of the fragility is related with the decrease of the strength of the connectivity between the structural units. Therefore, the analysis suggests that in the systems in consideration, the salt interrupts the connectivity of the polymeric chains. The results obtained here are consistent with the previous report.[10)]

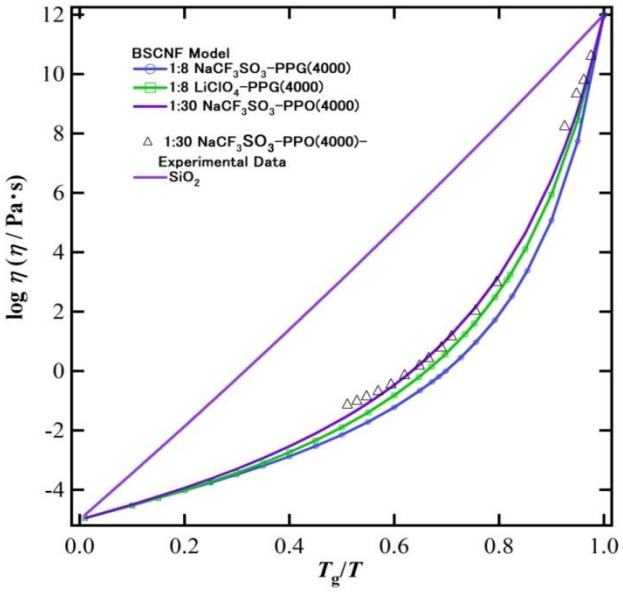

Fig. 3. Temperature dependence of the viscosity of polymer electrolytes described by Eq. (2.1). The behavior of SiO_2 is also shown for comparison.

§4. Conclusion

The BSCNF model and the WLF equation have been used to study the temperature dependence of the viscosity of polymer electrolyte systems. The result indicates that both models describe relatively well the experimental data. The analysis based on the BSCNF model suggests that by increasing the salt content, the fragility index increases due to the decrease of the connectivity between the structural units. From the comparison of these models, it was shown that the BSCNF model could provide a physical interpretation to the empirical parameters used in the WLF equation.

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