

CORRELATION BETWEEN THE TEMPERATURE RANGE OF COOPERATIVITY AND THE FRAGILITY INDEX IN ION CONDUCTING POLYMERS

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The effect of the plasticizer in the ion transport properties of a neat poly-(ethylene oxide), PEO-based ionomer, is investigated by the use of the bond strength-coordination number fluctuation (BSCNF) model of the viscosity. The plasticized forms of PEO-based ionomer considered contain 6 wt % of six miscible solvents with a wide range of dielectric constants. Recently, based on a relationship derived from the BSCNF that reproduces accurately the Vogel-Fulcher-Tammann (VFT) equation, we have proposed an expression for the fragility index dependence of the normalized temperature range of cooperativity $(T_c - T_k)/T_g$, where T_k is the Kauzmann temperature and T_c is a crossover temperature that demarcates two distinct dynamical regimes (low- T and high- T) above the glass transition temperature T_g . In the present work, the scope of such an expression is extended to the study of some ion conducting polymers. The values of the fragility index of the materials in consideration here are calculated from the VFT equation. These values of the fragility index enable us to evaluate the characteristic parameters B^* and C^* of the BSCNF for each material sample. The excellent agreement of the theoretical expression with the experimental data implies that by contrasting the PEO-based ionomer with plasticized forms, the normalized temperature range of cooperativity remains VFT-like. This result reinforces the idea that although the ionic conductivity increases dramatically with plasticization, the mechanism of ion transport remains unchanged.

Keywords: Fragility, Ion conducting polymer, Glass transition, Viscosity

1. Introduction

1.1. Background

Ion conducting polymers have recently received tremendous interest due to their technological importance in a wide variety of devices such as batteries, fuel cells, supercapacitors, sensors, organic light-emitting diodes, gate membrane for controlled release of anionic drugs, electrochemically switchable ion-exchanger for water purification, hybrid power sources, etc. [1-3]. So far, Fenton et al. [4] had reported the complexation of alkali metal salts with poly-(ethylene oxide) (PEO), but their technological significance was pointed out few years later by Armand et al. [5]. The basic requirements of polymer electrolytes to be used in devices are, among many others: high conductivity at room temperature, low electronic conductivity, good mechanical properties, thermal, chemical, electrochemical and photochemical stability added to an ease of processing [6-8]. Gel polymer electrolyte (GPE), characterized by a higher ambient ionic conductivity but poorer mechanical properties, is the essential component of the Li-ion batteries. Pure solid polymer electrolyte (SPE), composed of lithium salts dissolved in high molecular weight polyether host, provides major advantages such as leak proof, high-energy density, light weight, good mechanical stability, weak flammability, and low dendrite formation. Unlike the case of GPE, limited ambient ionic conductivity of SPE is a serious barrier of the materials in potential technological applications [9-16].

In order to combine good ambient ionic conductivity and good mechanical properties, several polymer electrolyte systems have been investigated. Among them, PEO has shown great potential as the best solvating medium for a variety of lithium salts in that, it easily solvates cations by interaction with the polar ether oxygen in the main chain and coordinates effectively with cations to form homogenous solutions. Although PEO shows high flexibility, good chemical, mechanical and electrochemical stability, the ionic conductivity at room temperature remains low, in the range of 10^{-8} to 10^{-5} S.cm⁻¹. This weak ionic conductivity can be explained by the low mobility of the ionic charges in the polymer matrix due to the mobility of both cations and anions, the low solubility of salt in amorphous phase, and the higher degree of crystallinity [6,17]. Out of all the methods used to enhance the ionic conductivity of PEO without affecting their mechanical properties, the addition of plasticizer has been most investigated [9].

1.2. Effect of the plasticizer in the ion transport properties of polymeric materials

The low viscosity, non-volatility, and polar nature of different plasticizers are excellent properties for their use in polymer electrolytes. Studies on the various properties of plasticized polymer electrolytes (PPE) reveal that the incorporation of plasticizer increases the amorphous content, dissociates the ion aggregates in polymer electrolytes at higher salt concentrations as well as decreases the glass transition temperature which in turn helps in an easy movement of the polymer chains, resulting in an increase in conductivity [11,18-20]. Depending on the PEO-based polymer in consideration, the conductivity enhancement with the addition of different plasticizers has been found to be related to the donor number, to the dielectric constant, or to the viscosity of the plasticizer. For instance, the addition of plasticizers such as propylene carbonate, ethylene carbonate, dimethylformamide, etc., with dielectric constants greater than that of PEO, to PEO-NH₄F polymer electrolytes has been found to result in an increase in conductivity, which further depends upon the concentration of salt as well as the amount of plasticizer. In opposite, the addition of plasticizers such as diethylcarbonate, dimethylcarbonate, etc., with dielectric constants lower than that of PEO, does not result in enhancement in conductivity [6]. It has also been found that the increase in conductivity is more for plasticizers with higher donor number [6,21].

Recently, the dielectric spectroscopy on a neat poly-(ethylene glycol)-based ionomer and six mixtures containing 6 wt % plasticizer with a wide range of dielectric constants has been conducted [9]. The solvents used were propylene carbonate (PC), dioctyl phthalate (DOP), dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), ethylene glycol (EG), and triethylamine (TEA). There, it has been found that the conductivity increases dramatically but remains Vogel-Fulcher-Tammann (VFT)-like for all plasticized ionomers. On the other hand, recently [22], a relationship that reproduces accurately the VFT equation has been derived based on the bond strength-coordination number fluctuation model of the viscosity [23]. By using such a relationship, we have derived an expression for the fragility index dependence of the normalized temperature range of cooperativity $(T_c - T_k)/T_g$ [24]. Here, T_k is the Kauzmann temperature and T_c is a crossover temperature that demarcates two distinct dynamical regimes (low- T and high- T) above the glass transition temperature T_g . A transition from a liquid-like to a solid-like dynamics on a molecular level appears at T_c . With the objective to gain further insight on the effect of the plasticizer in ionic conduction, we have investigated, in the light of our theory, the relationship between the fragility index of some ion conducting polymers and the temperature range of cooperativity. From such a study, we'll be able to confirm or not if the mechanism of ion transport remains unchanged, in view of the dramatic increase of the ionic conductivity with plasticization.

2. The theory of the fragility index dependence of the normalized temperature range of cooperativity

The temperature dependence of the viscosity has been defined in terms of the bond strength-coordination number fluctuation model as [23]

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

where

$$C = \frac{E_0 Z_0}{RT_g}, \quad B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2}, \quad \text{and} \quad x = T_g / T. \quad (2)$$

η_0 is the viscosity at high temperature limit considered here as material independent. Based on experimental data, the value of 10^{-5} Pa.s is commonly used [25]. The usual value of the viscosity at the glass transition temperature $\eta_{T_g} = 10^{12}$ Pa.s is adopted [25]. C contains information about the total bond strength of the structural unit and B gives its fluctuation. E_0 is the average value of the binding energy between the structural units and Z_0 is the average value of the coordination number of the structural units. ΔE and ΔZ are the fluctuations of E and Z , respectively. R is the gas constant. Recently, it has been shown that the VFT equation can be reproduced when the following expression is satisfied [22,26]

$$C = \frac{2\gamma(1-B)}{2\gamma + \sqrt{B}(1+\gamma^2)} \left\{ \ln(\eta_{T_g}/\eta_0) + \frac{1}{2} \ln(1-B) \right\}, \quad (3)$$

with

$$\gamma \equiv \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0} = 1. \quad (4)$$

The fragility index m can be expressed by the following well known formula [27, 28]

$$m = \lim_{T \rightarrow T_g} \frac{d \log \eta}{d(T_g/T)}. \quad (5)$$

According to the bond strength-coordination number fluctuation model, the relationship between the fragility index and the parameters B and C is given by [22,23,26]

$$m_{BC} = \frac{1}{\ln(10)} \left\{ \frac{B - C + 2 \left[\ln \left(\frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1-B) \right]}{(1-B)} \right\}. \quad (6)$$

Based on equations (3), (4) and (6), in our previous study [24], we have derived the following expression for the temperature range of cooperativity

$$\frac{T_c - T_k}{T_g} = \frac{1}{x_c} - \left[1 - \frac{\left(\frac{1 + \sqrt{B^*}}{1 - B^*} \right) C^* - \frac{1}{2} \ln(1 - B^*)}{m \ln(10)} \right], \quad (7)$$

where x_c and m represent the reduced inverse temperature T_g/T_c and the fragility index, respectively. B^* and C^* denote the values of B and C that obey equations (3) and (4). It is worth to note here that the Kauzmann temperature T_k has been considered similar to the ideal glass transition temperature T_0 appearing in the VFT equation [29], also known as Vogel temperature.

3. Application of the theory and discussion

So far, the description of dynamical critical phenomena in glass forming systems has been given by the mode-coupling theory (MCT) [30-32]. Although the applicability of the MCT still remains a subject of heated debates [33,34], it has been used by many researchers to investigate the temperature range above the glass transition temperature T_g . The MCT predicts the existence of a dynamic crossover, i.e., a transition from a liquid-like to a solid-like dynamics on a molecular level, at the critical temperature T_c . However, the experimental determination of the crossover temperature T_c is difficult [35]. In order to test the MCT predictions, various methods have been used. Among these, neutron and light scattering spectroscopy, dielectric relaxation, time-domain measurements by optical Kerr effect, and computer simulations. Novikov et al. [36] have collected the data of T_c for 26 different glass-forming systems including small molecules, polymeric materials, ionic systems, covalent systems, orientationally disordered crystals, etc. Analysis of all data shows that T_c scatters between $(1.10 - 1.71)T_g$, and particularly between $(1.14 - 1.35)T_g$ for polymeric materials. These data are expected to be close to those of MCT, but with some exceptions especially related to the α - β -splitting region and the characteristic relaxation time $\tau_{\alpha\beta}$ [36].

Indications for a change of diffusion mechanism in supercooled liquids have been given by Rössler, in term of the corresponding-states analysis of the viscosity [37]. There, it has been found that the crossover temperature T_c for different liquids should be approximately the same if a reduced inverse temperature scale T_g/T is used. Accordingly, the NMR correlation times, the tracer diffusion by Rayleigh forced scattering, the dielectric relaxation, and the electric conductivity for 1,3,5-*tri- α* -naphthyl benzene, $0.40\text{KNO}_3 \cdot 0.60\text{Ca}(\text{NO}_3)_2$, and $0.38\text{KNO}_3 \cdot 0.62\text{Ca}(\text{NO}_3)_2$ have been plotted as a function of T_g/T . It has been found that a transition occurs in a narrow range corresponding to $T/T_g = 1.20 - 1.28$. The NMR correlation times for α and β processes have also been plotted as a function of T_g/T for these three organic supercooled liquids: *o*-terphenyl, tricresyl phosphate, and toluene [37]. The results clearly showed that a bifurcation of the two relevant processes appears at $T/T_g = 1.18$. Petry et al. have obtained the same result by plotting the temperature dependence of the Debye-Waller factors for *o*-terphenyl [38]. Many authors, for instance Boyer and Miller [39], claimed that usually $T_c \approx (1.20 \pm 0.05)T_g$ for most polymeric materials.

As far as the authors are informed, the values of T_c for the materials in consideration here are not available in the literature. Thus, strengthened by the data collected by Novikov et al. [36], we will use this relationship in the case of our study. On the other hand, it is well known elsewhere in the literature that the temperature dependence of the viscosity can be described by the VFT equation given as

$$\eta = \eta_0 \exp \left[\frac{B_{VFT}}{T - T_0} \right], \quad (8)$$

where η_0 and T_0 are the viscosity at high temperature limit and the Vogel temperature, respectively. B_{VFT} is a constant. At the glass transition temperature limit T_g , the fragility index m_{VFT} can be derived from equations (5) and (8) as

$$m_{VFT} = \frac{1}{\ln(10)} \left[\frac{\left(\frac{B_{VFT}}{T_g} \right)}{\left(1 - \frac{T_0}{T_g} \right)^2} \right]. \quad (9)$$

By using the data of B_{VFT} , T_0 and T_g obtained by Klein et al. for a neat poly-(ethylene glycol)-based ionomer and plasticized forms [9], the values of the fragility index can be calculated. Thanks to equations (3), (4) and (6), these values of the fragility index enable us to evaluate the characteristic parameters B^* and C^* for each material sample. The behavior expressed by Eq. (7) is shown in Fig. 1 for different values of B^* and C^* taken in the scatter range of the values obtained for the materials in consideration. The plasticized ionomer's name is constituted by the plus sign followed by the solvent name. We can observe in the figure that the agreement with experimental data is excellent. It is shown that the higher the fragility index, the lower the normalized temperature range of cooperativity. This result has been reported by other authors via the correlation of the ratio T_c/T_g with the fragility index, m [36,40-42].

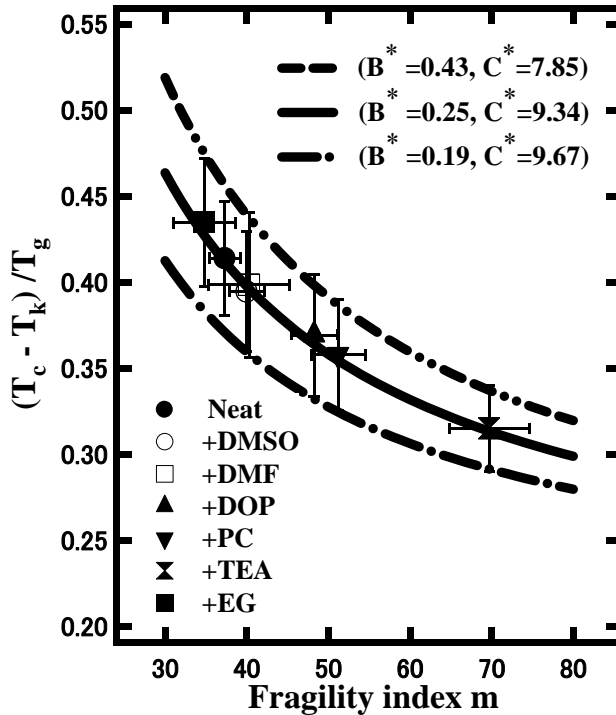


Fig 1. The normalized temperature range of cooperativity versus the fragility index in some ion conducting polymers.

According to Angell [41], liquid behavior during cooling is classified between "strong" and "fragile", and the basic properties of relaxing liquids are correlated through the fragility. The sudden change of slope occurring in the temperature dependence of the Debye-Waller factor, the mean square displacement of the system's particles, has been found in simple liquids and chain polymers. In these cases, the observed effect has been attributed to the onset of inelastic processes and has been interpreted in terms of MCT [38, 43,44]. Proteins seem to be both strong and fragile because they show a sharp boson peak change, around 200 K and which persists far above, in the temperature dependence of the Debye-Waller factor [45,46]. The separation of protein dynamics into β -phase (due to water-to-side chain interactions which become active at 170 K), and strong α -phase (associated with main chain motions that are responsible for the persistent boson peak at much higher temperatures) is probably the key to solve this paradox insofar as for some cases, the sudden loss of some liquid degrees of freedom through a weak first-order transition is evocative of the polyamorphic transition between native and denatured hydrated proteins. This transition can be interpreted as single-chain glass-forming polymers plasticized by water and cross-linked by hydrogen bonds. Moreover, the fragile ionic liquids may originate in strong anharmonicity, i.e. in large Gruneisen parameter of bosons modes. Thus, if the overdamping of the boson peak really triggers the glass transition, then the more anharmonic are the vibrations associated with this peak, the lower is the temperature (hence the closer to T_k) of the configuration space exploration should begin (at T_g) [41]. Strengthened by the fact that the ratio T_g/T_k scales with the liquid strength parameter, we can connect the fragility with the anharmonicity. In other words, the bosons modes may be connected to the Kauzmann temperature T_k and the fragility of the liquid. Based on these explanations and the result obtained, our study clearly indicates that the ionic conductivity of the neat PEO-based ionomer with plasticized forms exhibits the VFT-like behavior as suggested in Ref. 9.

It is relevant to note that for the high-quality conductivity data of the plasticized ionomers considered here, the glass transition temperature has been found to be the critical characteristic governing the ionic conductivity [9]. Moreover, it has been shown that the ionic conductivity has a slight but statistically negligible dependence on dielectric constant and donor number, no dependence on viscosity, and a strong dependence on the glass transition temperature. In this way, a conductivity master curve as a function of T_g - normalized temperature has been obtained. Fig. 1 clearly shows that the conductivity change can be entirely expressed by a change in T_g , within statistical errors, even if the plasticizers are changed. Other than the change in the glass transition temperature by plasticization, the ionic conductivity varies weakly and randomly with the donor number. For instance, at a common temperature of 0°C for the solvents DMF, DOP, PC, TEA, DMSO, and EG, the donor numbers have been found to take the values of 27, 22, 15, 61, 30, and 4, respectively. In the same order as that of the solvents, the ionic conductivity has been found to increase as 0.96, 4.1, 62, 71, 179, and 181 ($\times 10^9$ S/cm) [9]. Even if there is no general trend between the donor number and the ionic conductivity, we can nevertheless observe that the highest value of the conductivity is obtained for the lowest value of the donor number.

4. Conclusion

The relationship between the fragility index of some ion conducting polymers and the temperature range of cooperativity has been studied theoretically. It has been found that the higher the fragility index, the lower the normalized temperature range of cooperativity. A low value of the fragility index corresponds to strong molecular interactions, while a high value corresponds to weak molecular interactions. This result supports the picture that the kinetic properties of glass forming liquids, as given by the fragility index, and the cooperative molecular relaxations of the formed glass are correlated. The excellent agreement of our theory, which reproduces accurately the VFT equation, with the data for the neat and plasticized ionomers obtained from VFT fits enable us to reinforce the idea that the mechanism of ion transport remains unchanged although the ionic conductivity increases dramatically with plasticization.

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