

INFLUENCE OF PEG-BORATE ESTER ON THERMAL PROPERTY AND IONIC CONDUCTIVITY OF THE POLYMER ELECTROLYTE

Y. Kato¹, K. Hasumi¹, S. Yokoyama², T. Yabe², H. Ikuta¹, Y. Uchimoto¹ and M. Wakihara^{1}*

¹Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

²Alkylene Oxide Group 2, Oleochemicals Research Lab., NOF corporation, 3-3 Chidori-cho, Kawasaki-ku, Kawasaki, Kanagawa 210-0865, Japan

Abstract

We have focused on the poly(ethylene glycol) (PEG)-borate ester as a new type plasticizer for solid polymer electrolyte for lithium ion secondary battery. Adding the PEG-borate ester into the electrolyte shows the increase in the ionic conductivity of the polymer electrolyte. By measuring the glass-transition temperature of the polymer electrolytes with DSC, it is found that the increase in ionic conductivity of the polymer electrolyte is due to the increase in ionic mobility. By investigating the temperature dependence of the ionic conductivity of the polymer electrolytes using William–Landel–Ferry type equation, we considered that the PEG-borate ester does not have any influence for dissociation of Li-salt.

Keywords: glass-transition temperature, ionic conductivity, PEG-borate ester, polymer electrolyte, WLF plot

Introduction

Polymer electrolyte in which lithium ions conduct has attracted much attention because of their practical application such as lithium secondary batteries, sensors and display devices [1–4]. However, the ionic conductivity of polymer electrolyte has not reached sufficient level for the practical applications because of low mobility of lithium ions in the electrolytes. In order to improve the ionic conductivity of the polymer electrolyte, addition of low-molecular mass non-aqueous organic solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) into matrix polymer as a plasticizer has been proposed [5–8]. These solvents are helpful in getting sufficient high ionic conductivity even at room temperature to polymer electrolyte; however, they have some problems for application to lithium ion battery that they are volatile and flammable. In the meanwhile, addition of poly(ethylene glycol)

* Author for correspondence: E-mail: mwakihar@o.cc.titech.ac.jp

(PEG) oligomer into poly(ethylene oxide) (PEO)-based polymer electrolyte has been studied [9–12], and recently, Abraham *et al.* have suggested the addition of the PEG oligomer as a plasticizer into the PVdF–HFP copolymer-based polymer electrolyte where they call this system ‘PEO-like’ polymer electrolyte [13, 14]. We have focused on the PEG-borate ester as a new type plasticizer for polymer electrolyte and shown that the PEG-borate ester is helpful for getting high ionic conductivity more than 10^{-4} S cm^{-1} at room temperature and, simultaneously, has high safety because of high flash point [15, 16]. However, the influence of the addition of the PEG borate ester on the thermal property of polymer chains in polymer electrolyte, for example crystallinity or glass-transition temperature, has not been clarified in detail including the relation with ionic conductivity.

In the present study, we have studied the influence of the addition of PEG-borate ester on the thermal property of polymer electrolyte based on PEG-metacrylate and the relation between the property and the ionic conductivity of the electrolyte. Especially, in the present paper, we report the influence of the PEG-borate ester on glass-transition temperature and ionic conductivity of the polymer electrolytes by using William–Landel–Ferry (WLF) type relationship.

Experimental

PEG-borate ester whose EO chain length (n) is equal to 6, as shown in Fig. 1, was used as a plasticizer. The synthesis method of the PEG-borate ester was reported in the previous paper [16]. The matrix polymer was a copolymer of two types of poly(ethylene glycol) methacrylates, PDE600 and PME4000, supplied from NOF Co. Ltd. as shown in Fig. 2. The matrix polymer was synthesized by radical polymerization of the mixture of PDE600 and PME4000 (1:1 by mass ratio) by using azobisisobutyronitrile (AIBN) as an initiator. Lithium bis-trifluoromethanesulfonimide (LiTFSI) (Fluka Co. Ltd.) for lithium salt was used as received.

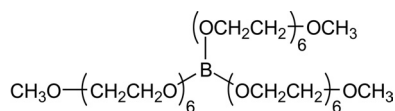


Fig. 1 Structural formula of PEG-borate ester

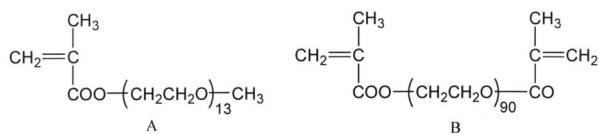


Fig. 2 Structural formulas of poly(ethyleneglycol) methacrylate: A – PDE600; B – PME4000

The polymer electrolyte films were prepared by the following procedure. At first, appropriate amounts of PDE600, PME4000, PEG-borate ester and LiTFSI were mixed together in a flask and stirred for 3 h. The molar ratio of lithium atoms to ether

oxygen atoms in the total polyethers of PDE600, PME4000 and PEG-borate ester was fixed to 1:8. The resulting homogeneous viscous solution was poured on a Teflon plate and then a small amount of AIBN was added as an initiator for radical polymerization of matrix polymer. By heating the solution on the plate at 60°C for 2 h to polymerize, free-standing electrolyte films of about 1 mm thickness were obtained after cooling to room temperature. All these steps of the preparation were carried out in Ar-filled glove box (dew point: -76°C).

Ionic conductivity of the polymer electrolytes was measured by the AC impedance technique using a computer controlled Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 to 13 MHz. The polymer electrolyte film was cut into disks of 10 mm in diameter, sandwiched with stainless steel electrodes (SUS 304) and subjected to the impedance analyzer.

Thermal property of the obtained polymer electrolyte samples was investigated by differential scanning calorimetry (DSC) using DSC 220C (Seiko Instruments). After the sample in aluminum pan was cooled to -120°C at the scan rate of 10°C min⁻¹, the measurement was carried out from -120 to 100°C at the same scan rate. An empty aluminum pan was used as a reference.

Results and discussion

Figure 3 shows the temperature dependence of the ionic conductivity, represented in Arrhenius type, for the polymer electrolyte sample, PDE600 :PME4000:PEG-borate ester ($n=6$)=1:1:5+LiTFSI (Li/EO=1/8), and the sample without the PEG-borate ester as a reference. The drastically increase in ionic conductivity was observed by adding the PEG-borate ester as a plasticizer to the matrix polymer. Additionally, both of the Arrhenius plots of the ionic conductivity exhibited convex-profile. This result indicates that the ionic conduction mechanism of both samples, containing PEG-borate ester and without the one, cannot be expressed by the hopping model of carrier ions, which is applied to inorganic ionic conductors [17] or gel polymer electrolytes used with low molecular solvents, such as PC, EC and DMC [18]. This type of temperature

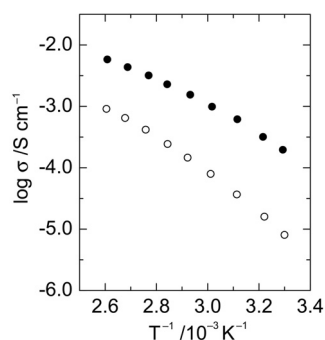


Fig. 3 Arrhenius plots of ionic conductivity for PDE600:PME4000:PEG-borate ester (1:1:5)+LiTFSI (Li/EO=1/8). ● – with PEG-borate ester, ○ – without PEG-borate ester

dependence is typically observed in case of ionic conduction in solid polymer electrolyte, which is indicative of the ionic conduction mechanism expressed by William–Landel–Ferry (WLF) relationship [19]. It is generally considered in polymer electrolyte that ionic conduction occurs by segmental motion of polymer chains in amorphous region [20–24]. When ionic conduction mechanism does not obey the hopping model but the free volume theory, which is correlated with segmental motion of polymer chains, the temperature dependence of ionic conductivity does not follow Arrhenius type relationship but WLF (William–Landel–Ferry) type [25–28].

In order to clarify the conduction mechanism in the present system, we examined thermal property and the glass-transition temperature (T_g) of the polymer electrolyte samples by DSC. Figure 4 shows DSC curves of the polymer electrolyte containing the PEG-borate ester and that without PEG-borate ester (the composition of the polymer electrolyte is equal to that of the samples in Fig. 3). When the PEO region in the polymer electrolyte has crystallized region, an endothermic peak which is due to melting of the crystallized region is observed around 60°C [29–31]. However, as shown in this figure, there are not any peaks in the polymer electrolyte samples. Therefore, it is confirmed that the polymer electrolyte samples do not have crystallized regions and most of the polymer electrolytes is considered to be amorphous. In the meantime, glass-transition of these samples was observed in each curve around –50°C. The glass-transition temperature, T_g , was taken at the center of the heat capacity change encountered during the transition.

From the DSC curves in Fig. 4, T_g of the polymer electrolyte samples were determined and listed in Table 1. As described before, the ion conduction occurs by segmental motion of polymer chains. T_g is correlated with flexibility of EO chains, i.e. T_g is correlated with segmental motion of EO chains. Accordingly, it is considered that mobility of carrier ions is correlated with T_g . For example, when T_g of the polymer electrolyte is low, the ionic mobility of the carrier ions in the electrolyte is expected to be high [32–34]. As seen in Table 1, it was observed that T_g of the sample decreased by adding the PEG-borate ester into the polymer electrolyte and, accordingly, the ionic mobility of the electrolyte is expected to increase.

According to the free volume theory [19], WLF equation is represented as follows:

$$\log \frac{\sigma(T)}{\sigma(T_g)} = \frac{C_1(T-T_g)}{C_2+(T-T_g)} \quad (1)$$

where $\sigma(T)$ and $\sigma(T_g)$ are the conductivity at temperature T and T_g , respectively, and C_1 , C_2 the WLF parameters of ionic conductivity. However, the ionic conductivity at T_g , $\sigma(T_g)$, is difficult to measure in the present experiments because $\sigma(T_g)$ is very low to measure by the complex impedance measurement and, therefore, 30°C was selected as reference temperature, T_0 . Equation (1) is rewritten as follows:

$$\log \frac{\sigma(T)}{\sigma(T_0)} = \frac{C'_1(T-T_0)}{C'_2+(T-T_0)} \quad (2)$$

The parameters in Eq. (1) are calculated from [26]:

$$C_1 = \frac{C'_1 C'_2}{C'_2 - (T_0 - T_g)} \quad (3)$$

$$C_2 = C'_2 - (T_0 - T_g) \quad (4)$$

In order to investigate the ionic conduction mechanism of the polymer electrolyte samples, WLF parameters and $\sigma(T_g)$ are required. Figure 5 shows WLF plots of ionic conductivity for the polymer electrolyte samples. From the inverse of Eq (2), temperature dependence of the ionic conductivity is plotted as $\log[\sigma(T)/\sigma(T_0)]$ vs. $1/(T-T_0)$. It was observed as seen in Fig. 5 that $\log[\sigma(T)/\sigma(T_0)]$ is in proportion to $1/(T-T_0)$. This result indicates that the temperature dependence of the ionic conductivity for each sample follows the WLF-type equation.

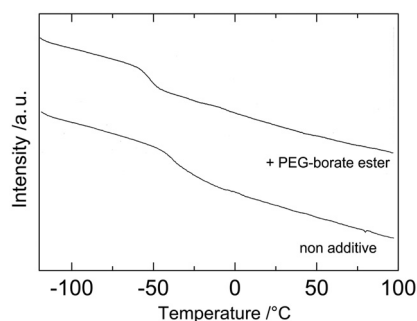


Fig. 4 DSC curves of PDE600:PME4000:PEG-borate ester (1:1:5)+LiTFSI (Li/EO=1/8)

Table 1 σ at 30 and 60°C, and T_g of PDE600:PME4000:PEG-borate ester (1:1:5)+LiTFSI (Li/EO=1/8)

Additive	$\sigma/S \text{ cm}^{-1}$ at 30°C	$\sigma/S \text{ cm}^{-1}$ at 60°C	$T_g/^\circ\text{C}$
–	$8.16 \cdot 10^{-6}$	$8.05 \cdot 10^{-5}$	–36.3
PEG B-ester	$1.96 \cdot 10^{-4}$	$9.88 \cdot 10^{-4}$	–49.1

The WLF parameters, C_1 , C_2 and $\sigma(T_g)$ were calculated from Fig. 5 and Eqs (2)–(4) and then listed in Table 2. As compared to the universal values of WLF parameters, $C_1=17.4$ and $C_2=51.6$ /K [19], the obtained parameters were found to be close to those which implies that the temperature dependence of ionic conductivity was dominated by that of ionic mobility correlated with the segmental motion. In the meantime, since the segmental motion of polymer chains is frozen at the glass-transition temperature, it is considered that ionic conductivity at that temperature strongly reflects the concentration of the carrier ions in the polymer electrolyte. Accordingly, the difference of the ionic conductivity at each glass-transition temperature of the polymer electrolyte containing Li-salt at an equal concentration reflects the difference of the concentration of the carrier ions, i.e. the difference in the degree

of Li-salt dissociation. As seen in Table 2, $\sigma(T_g)$ of the sample containing the PEG-borate ester is the same order of magnitude as that of the sample without PEG-borate ester. Therefore, it is considered that the PEG-borate ester does not have any influence on dissociation of Li-salt.

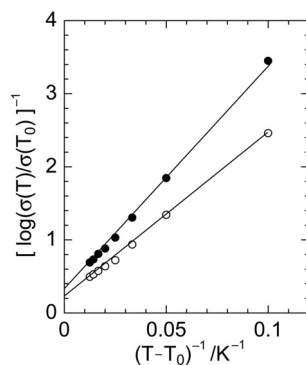


Fig. 5 WLF plots of ionic conductivity for PDE600:PME4000:PEG-borate ester (1:1:5)+LiTFSI (Li/EO=1/8). ● – with PEG-borate ester, ○ – without PEG-borate ester

Table 2 WLF parameters of PDE600:PME4000:PEG-borate ester (1:1:5)+LiTFSI (Li/EO=1/8)

Additive	$T_g/^\circ\text{C}$	$C_1/-$	C_2/K	σ at $T_g/\text{S cm}^{-1}$
–	–36.3	11.8	52.5	$3.07 \cdot 10^{-12}$
PEG B-ester	–49.1	11.1	40.8	$7.72 \cdot 10^{-12}$

Conclusions

We investigated the influence of the PEG-borate ester on the thermal property of polymer electrolyte based on PEG-methacrylate and the relation between the property and the ionic conductivity of the electrolyte. It was found by comparing T_g of the polymer electrolyte samples that the ionic mobility is expected to increase. Additionally, by investigating the ionic conductivity at the glass-transition temperature, the PEG-borate ester does not have any influence on dissociation of Li-salt. Therefore, we conclude that the increase in ionic conductivity by adding the PEG-borate ester into the polymer electrolyte is mainly due to the increase of the ionic mobility of the carrier ions in the polymer electrolyte.

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