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Molten lithium sulfonimide salt having poly(propylene oxide) tail

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Abstract

Poly(propylene oxide) (PPO) tailed lithium(trifluoromethyl sulfonylimide)s (TFSI–PPO) were prepared as non-onium type ionic liquid polymers. Introduction of PPO chain to the TFSI salt group resulted in lower the glass transition temperature (T_g) and induce the salt dissociation. The TFSI–PPO showed relatively high ionic conductivity owing to the high dissociation degree of the TFSI salt group. The maximum ionic conductivity of 3.3×10^{-6} S cm^{-1} was observed at 30 °C for TFSI salt having PPO tail with number average molecular weight of 850. On the other hand, PPOs having the same salt moiety on both chain ends ($(TFSI)_2$–PPO) showed higher T_g than that of TFSI–PPOs. The lithium transference number of the $(TFSI)_2$–PPO with PPO chain length of Mn = 2000 was 0.74 in spite of slightly lower ionic conductivity.

Keywords: Ionic liquid; Poly(propylene oxide); Polyether/salt hybrid

1. Introduction

Recent development of ionic devices has been stimulating a number of researchers to study electrolyte materials [1]. In search for highly conductive electrolyte material, various types of ion conductive polymers have been widely investigated [2–4]. The ion conductive polymer is typically represented by poly(ethylene oxide) (PEO) derivatives, which is composed of high density of polar groups. PEO derivatives are known to form complexes with a wide variety of salts, showing ionic conductivity of 10^{-4}–10^{-7} S cm^{-1} at ambient temperature.

On the other hand, in recent years, ionic liquids have been earnestly studied as a new family of ion conductive materials [5–7] because of their unique features, i.e. no volatility, high decomposition temperature, and high ionic conductivity of over 10^{-2} S cm^{-1}. The most widely investigated ionic liquid is di-alkyl imidazolium salt having soft counter anion such as BF_4^- and PF_6^-. Ionic liquids possess enough polarity to dissolve lithium salts, however, in these systems, ionic species that constitute the matrix also migrate along the potential gradient.

As an approach to develop a new family of non-onium type ionic liquid, we have reported the synthesis of molten salts (carboxylate [8], sulfonate [9], and sulfonamide salts [10]) bearing covalently bonded PEO tail (PEO/salt hybrids; Mn = 400–1000). However, in crystalline state (Mn > 1000), the ionic conductivities of PEO/salt hybrids were below 10^{-8} S cm^{-1}. To overcome this drawback, we have prepared a series of poly(propylene oxide) (PPO)/salt hybrids, since PPO is known to show no crystallinity. The obtained PPO/trifluoromethyl sulfonamide (TFSA) salt hybrid showed ionic conductivity over 10^{-6} S cm^{-1} at room temperature [11].

In this work, in order to further improve the ionic conductivity, highly dissociative lithium trifluoromethyl sulfonylimides (TFSI) [12], [13] having PPO tail were prepared (Fig. 1).

2. Experimental

2.1. Materials

PPOs having sulfonyl chloride groups on their chain ends were prepared by the reaction of PPO having sulfonate end group with thionylchloride [14]. Trifluoromethyl sulfonamide and triethylamine were purchased from Tokyo Kasei Kogyo. Co. Ltd, and were used as received. Lithium methoxide, 1.0 M solution in methanol was purchased from

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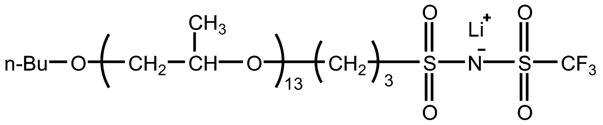


Fig. 1. Structure of TFSI–PPO$_{850}$.

Aldrich, and used as received. Acetonitrile and chloroform were purchased from Wako Pure Chemicals Co. Ltd.

2.2. Synthesis

Synthesis and evaluation of PPO/TFSI salt hybrids were carried out under dry nitrogen or argon atmosphere. The synthesis of PPO/TFSI lithium salt hybrid (Mn of PPO = 850) was typically carried out as follows. To a homogeneous solution of α-butyl PPO having sulfonyl chloride group on the ω chain end (5.0 g) and trifluoromethyl sulfonamide (0.75 g) in acetonitrile, triethylamine (1.1 g) was added, and the mixture was stirred for 12 h at 60 °C. After removing the solvent, the residue was added ether, and then the insoluble part was eliminated by filtration. Lithium methoxide was added to the filtrate and the reaction mixture was stirred for 8 h. The solvent was removed, and the resulting viscous liquid was dissolved in the chloroform. The obtained suspension was filtrated. The solvent of the filtrate was removed to give a slightly yellow, viscous liquid in 70% yield. The structure was confirmed by ^{19}F NMR and FT-IR spectra. The ^{19}F NMR of the polymer is shown in Fig. 2.

^{19}F NMR (δ, ppm): -79.6(s)

IR spectra (cm^{-1}): 2972, 2928, 2868, 1650, 1454, 1374, 1342, 1262, 1114, 1014, 972, 932, 884, 824, 780, 750.

A variety of TFSI–PPO$_n$s (‘n’ stands for Mn of the PPO segment) having α-butyl PPO (Mn = 350, 850, and 1100) were prepared in a similar manner using PPO of various chain length. (TFSI)$_2$–PPO$_n$s having TFSI groups on both PPO chain ends were also prepared using α,ω-(chlorosulfonyl) PPO (Mn = 400, 1200, and 2000) instead of α-butyl, ω-(chlorosulfonyl) PPO.

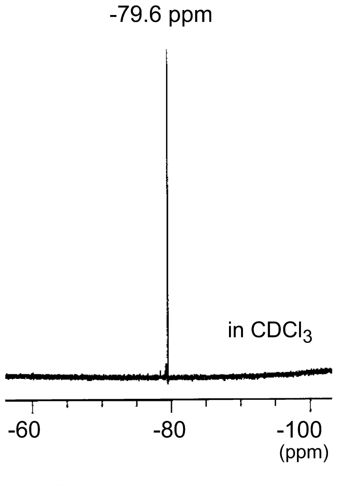


Fig. 2. ^{19}F NMR spectra of TFSI–PPO$_{850}$.

2.3. Methods

The thermal properties of the samples were evaluated with a differential scanning calorimeter, SEIKO instruments Inc., DSC220. The sample was cooled down to -140 °C, and then DSC scanning was carried out up to 150 °C at the heating rate of 5 °C min^{-1}.

The ionic conductivity was measured by means of complex impedance method on Schlumberger Solartron-1260 impedance/gain phase analyzer over frequencies range from 10 Hz to 1.0 MHz. The sample was sandwiched in a custom designed cell constructed with a pair of stainless steel (SUS) plates and a polypropylene spacer. This spacer defines the cell constant of 500 μm thick and 0.283 cm^2 area. The temperature of the cell was swept from 60 to 10 °C at the sweeping rate of 2 °C min^{-1}, while the impedance data for each temperature was collected using custom designed apparatus. The dc polarization current in the sample was measured by applying 10 mV bias to a Li|sample|Li cell in which 100 μm thick lithium foils were put on stainless steel electrodes.

3. Results and discussion

All the PPO/TFSI salt hybrids were obtained as viscous liquids. During the DSC measurement, no melting point was observed for each sample, showing that they were amorphous. It is known that micro order phase separation of undissociated salts is generally observed for simply mixed PPO/low molecular weight salt systems [15], [16]. However, in the present hybrid systems, neither recrystallization nor phase separation of salts was observed, in accordance with the observed monomodal T_g peak in the DSC diagrams.

Fig. 3 shows the temperature dependence of ionic conductivity for TFSI–PPO. Among the evaluated systems, TFSI–PPO$_{850}$ showed the maximum ionic conductivity of 3.3×10^{-6} S cm^{-1} at 30 °C. The T_g of PPO/TFSI salt hybrid oligomer increased with decreasing the molecular

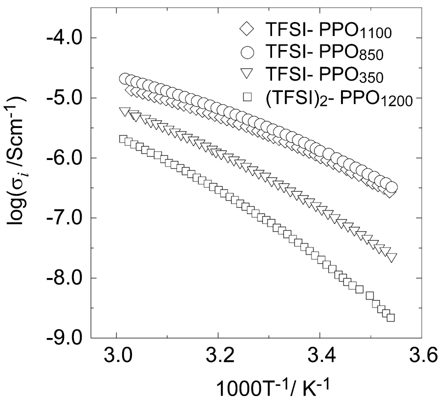


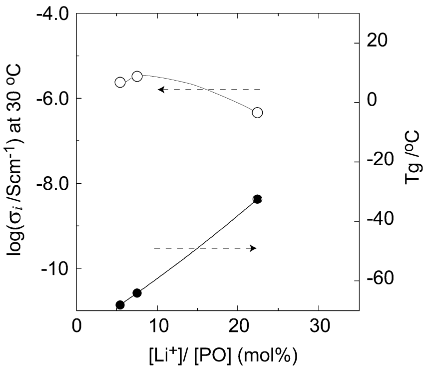
Fig. 3. Temperature dependence of the ionic conductivity for a series of (TFSI)$_{1\text{ or }2}$–PPO hybrids.

weight of PPO tail, i.e. with increasing of the salt concentration (Fig. 4(a), -32.5 °C; TFSI–PPO$_{350}$ $>$ -64.1 °C; TFSI–PPO$_{850}$ $>$ -68.1 °C; TFSI–PPO$_{1100}$). The appropriate salt concentration and low T_g of TFSI–PPO$_{850}$ system might have led to the relatively high ionic conductivity.

The ionic conductivity of (TFSI)$_2$–PPO systems was lower than that of TFSI–PPO systems. TFSI–PPO showed significantly lower T_g compared with (TFSI)$_2$–PPO as shown in Fig. 4 (-45.0 °C; (TFSI)$_2$–PPO$_{2000}$ $>$ -68.1 °C; TFSI–PPO$_{1100}$), in spite of quite similar salt concentration in both systems. It is known that ions tend to aggregate each other in polyether matrix, to form ion pairs or further aggregated species [17]. In the case of (TFSI)$_2$–PPO systems having salt structure on both chain ends, such ion aggregation on both chain ends should restrict the segmental motion and induce the rise of T_g. A relatively high T_g of (TFSI)$_2$–PPO system probably be explained by assuming this effect.

Fig. 5 shows the temperature dependence of the ionic conductivity for a series of PPO/salt hybrids (Mn of the PPO moiety is 2000) having various lithium salt structures such as TFSI, methyl sulfonimide (MSI) and methyl sulfonamide (MSA) [11] at the chain ends. Among these PPO/salt hybrids, (TFSI)$_2$–PPO$_{2000}$ showed the maximum conductivity of 1.2×10^{-6} S cm^{-1} at 30 °C. On the other hand, MSI and MSA salt system showed ionic conductivity of below 10^{-7} S cm^{-1}, although T_g of these systems (below -65 °C) was much lower than that of (TFSI)$_2$–PPO$_{2000}$ system (-45 °C). Since TFSI anion is known to have plasticizer effect for most polymer electrolytes, this elevation of T_g of TFSI–PPO was not explained fully. However, the T_g of PPO chain is low enough to neglect such effect. Instead, the contribution of pseudo cross-linking by the Li$^+$ and polyethers is effective to elevate the T_g because LiTFSI unit shows high degree of dissociation providing larger amount of Li$^+$ cations. The improved conductivity of (TFSI)$_2$–PPO$_{2000}$ system might also be elucidated by considering higher degree of dissociation of lithium TFSI.

(a) TFSI-PPO



(b) (TFSI)$_2$-PPO

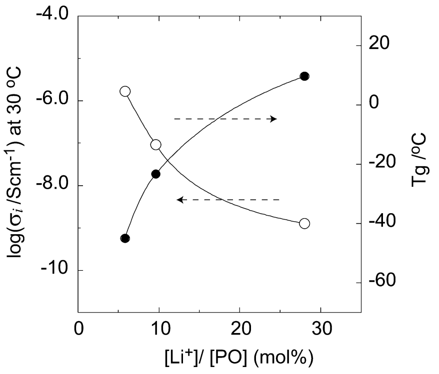


Fig. 4. Effect of PPO chain length on both the ionic conductivity and the glass transition temperature of (TFSI)$_{1\ \mathrm{or}\ 2}$–PPO hybrids. (a) TFSI–PPO and (b) (TFSI)$_2$–PPO.

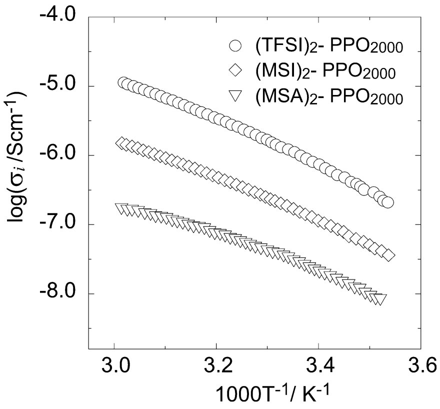


Fig. 5. Temperature dependence of the ionic conductivity for PPO/salt hybrids having a variety of salt species on both chain ends, with PPO chain length of Mn = 2000.

In polyether/salt hybrid systems previously reported by us, relatively high lithium ion transference number (t_{Li}^+) over 0.7 was observed because anionic charge is anchored to the oligomer chain end [11]. Fig. 6 shows the time dependence of dc polarization current in the Li|(TFSI)$_2$–PPO$_{2000}$|Li cell system. After the measurement was started, it took 5 h for the current to be stabilized. This stable current of 45 nA had been constantly observed for more than 20 h. The lithium transference number of this system was calculated according to the Vincent's equation [18], where $I(0)$ is the initial current, $I(\mathrm{s})$ is the stable current measured by the dc polarization method. R_0 and R_s are charge transfer

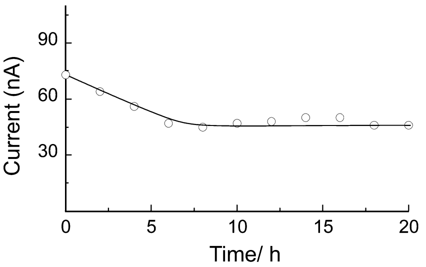


Fig. 6. Time dependence of the current under dc polarization for (TFSI)$_2$–PPO$_{2000}$.

resistance for initial and steady state, respectively. These values are obtained from the ac impedance measurement.

$$t_+ = \frac{I(\mathrm{s})[\Delta V - I(0)R_0]}{I(0)[\Delta V - I(\mathrm{s})R_\mathrm{s}]} \tag{1}$$

As results of these measurements, the lithium transference number was calculated to be 0.74 for $(\mathrm{TFSI})_2$–PPO_{2000}.

In spite of design of single ionic characteristics, cation transference number remained 0.74 in this case. This can be attributed to the contribution of anion migration since there is some portion of low molecular weight fraction of $(\mathrm{TFSI})_{1\ \mathrm{or}\ 2}$–PPOs. Additionally, the radius of gyration of $(\mathrm{TFSI})_{1\ \mathrm{or}\ 2}$–PPO anion might be not so large in bulk allowing the migration. The transference number decreased with decreasing the PPO chain length, suggesting the increased contribution of $(\mathrm{TFSI})_{1\ \mathrm{or}\ 2}$–PPO anion. In any case, it is extremely difficult to realize single ionic characteristics (i.e. transport only lithium ion in this case) in liquid systems, which is, however, easy to obtain in high molecular weight solid systems.

4. Conclusion

PPO/TFSI salt hybrids were prepared as viscous liquids without crystallinity. TFSI–PPO systems showed relatively high ionic conductivity over $10^{-6}\ \mathrm{S\ cm^{-1}}$ at room temperature according to the high dissociation degree of the TFSI salt group and low T_g. The lithium ion transference number of 0.74 for $(\mathrm{TFSI})_2$–PPO_{2000} is supposed to be one of the highest value as ionic liquid, and is also much higher than those for ordinary polyether salt mixed systems (~0.2).

Acknowledgements

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