High lithium ionic conductivity of poly(ethylene oxide)s having sulfonate groups on their chain ends[†]

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Poly(ethylene oxide) oligomers having sulfonate groups on one or both chain ends [PEO–$(SO_3M)_n$ ($n = 1$ or 2); M = Li, Na, K, Rb or Cs] with different PEO molecular masses (150–2000) have been prepared as new single-ion conductive matrices. High lithium ionic conductivity (4.45×10^{-6} S cm^{-1}, at 30 °C) was obtained in PEO–SO_3Li with PEO molecular mass of 350, the transport number of lithium ion (t_{Li^+}) was *ca.* 0.75 at 20 °C. The glass transition temperature (T_g) of these hybrid salts depended significantly on the molecular mass of the PEO and its molecular structure. The PEO oligomers containing a sulfonate group on only one end showed higher ionic conductivity than those containing sulfonate groups on both ends at the same salt fraction up to 50% per OE unit (*i.e.* $M_w > 500$). In both types of hybrid salts, the PEO–sulfonate with relatively high molecular mass around 2000 showed a crystalline phase at room temperature reflecting the crystallinity of the PEO component. On the other hand, the hybrid having PEO with low molecular mass of *ca.* 200 showed an amorphous phase but had a very high T_g, considerably reflecting the characteristics of the salt unit. PEO–sulfonates with molecular masses of PEO between 350 and 1000 were confirmed not only to show an amorphous phase over a wide temperature range but also to have low glass transition temperatures at *ca.* −40 °C.

Many ion-conductive polymer systems have been investigated mainly to improve their lithium ion conductivity for use in rechargeable polymer batteries.[2–4] Most prototype ion conductive polymers have been prepared by dissolving inorganic salts into polyether matrices. Polyether oligomers and their derivatives have been frequently used as ion conductive matrices, because they solubilize a significant quantity of inorganic salts in the bulk.[5] However, it is quite difficult to provide a large amount of carrier ions homogeneously whilst retaining high mobility, the addition of a large amount of salt into polyethers inducing an increase in the glass transition temperature (T_g) of the matrix.[6,7] Some interesting systems have been proposed recently in order to suppress an increase of T_g. Angell *et al.* prepared an 'ionic liquid' by mixing a small amount of polyether with a large amount of inorganic salt.[8] This system was based on the phenomenon that some types of mixed salt system enabled T_g to be low enough to show high ionic conductivity even after adding a small amount of polyether. On the other hand, other unique types of ion-conductive polymers were also prepared using a hyper-branched system,[9] a comb-shaped flexible polymer system containing poly(phosphazene),[10,11] and a polyether network system.[12–15] These systems were suitable in providing high ionic conductivity upon dissolving highly dissociable salts with low lattice energy such as $LiClO_4$ and lithium trifluoromethanesulfonimide (LiTFSI). However, all these were typical biionic systems; single-ion conductors are favorable in power sources since anion polarization usually induces unfavorable results. Mobility control of counter anions had not, as yet, been achieved for several new salts, *e.g.* LiTFSI.

On the other hand, while several cation-conducting systems have been prepared, ionic conductivity of single-ionic systems has not been improved substantially. Although it was easy to prepare single-ionic conductors by mixing polyanions and polyether oligomers,[15–18] they did not show good conductivity or stability. In a further development, charged groups such as carboxylate,[18–21] sulfonate,[22] and phenolate[23] were directly bound to the end of side-chains of comb-shaped polymers. Even in these systems, the lithium ionic conductivity was limited to *ca.* 10^{-7} S cm^{-1} in the bulk at room temperature.[20] Recently, Armand and co-workers prepared a high cation-conducting system which was prepared by the introduction of perfluorosulfonate groups into the polyether network.[24] In this system, the ionic conductivity increased with increase of the cation radius, however, the lithium ionic conductivity was low at *ca.* 10^{-5} S cm^{-1} even at 80 °C.

In order to obtain a matrix containing a large amount of carrier cations as well as high cation mobility, we prepared PEO/salt hybrids as a new cation-conducting system. Our α,ω-dicharged PEO oligomers consist of PEO with average molecular mass from 350 to 4000 and charged group(s) on the chain end(s) to delineate the effect of the molecular mass of PEO and charged group species. Since the anion site was fixed on the PEO chain end, the anion mobility was estimated to be much smaller than that of the cations. Furthermore, a totally amorphous phase was obtained when the PEO had a suitable molecular mass.[25] We have already reported the ionic conductivities and the properties of PEO oligomers with carboxylate[25,26] and benzenesulfonate groups[27] in detail. Here, we introduced highly dissociable sulfonate groups onto the PEO chain ends to improve the lithium ionic conductivity in the bulk. Terminal sulfonated PEO oligomers have already been prepared by several groups. Guyot and co-workers prepared PEO oligomers with sulfonate ends with a molecular mass of 1500 as an electrolyte for PEO oligomers.[28] The bulk ionic conductivity for PEO–sulfonates had not been reported except for PEO oligomers with M_w of 2000. Smid and coworkers prepared sulfonated-PEO oligomers of different molecular masses by the reaction of PEO oligomers and 1,3-propane sultone[29] but detailed conductivity data were not reported. Xu and Angell prepared similar sulfonated-PEO oligomers with a molecular mass of *ca.* 200.[30] Their hybrid had too high a T_g to show adequate conductivity in the bulk at room temperature. As far as we are aware, neither the effect of molecular mass of PEO on the phase characteristics nor the effect of cationic species on the ionic conductivity have been studied for sulfonate PEO derivatives in detail. We have already found that the T_g of PEO/salt hybrids is mainly governed by the molecular mass of the PEO and its terminal structure and the optimum molecular mass was found to be in the range 350–4000. In order to analyse the relation between the phase and its ionic conductivity in PEO–sulfonates, we prepared two types of PEO–sulfonate and analysed in detail the effect of the

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[†] Polymer/salt hybrid Part VIII, Part VII is ref. 1.

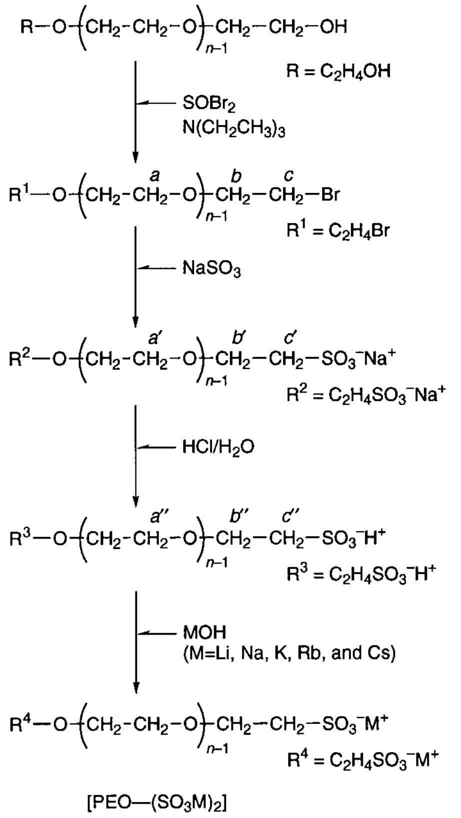
molecular mass of the PEO and the nature of the charged group on the ionic conductivity.

Experimental

Materials

Poly(ethylene oxide) (PEO) oligomers with average molecular masses of 200, 400, 600, 1000 and 2000 were purchased from NOF Co. Ltd. Monomethyl ether PEO oligomers (PEOM) with average molecular masses of 150, 350, 550, 750, and 2000 were purchased from Aldrich. Reagent-grade thionyl bromide was purchased from Aldrich and reagent-grade triethylamine and hydrochloric acid were purchased from Kanto Chem. Co. Ltd.

PEO oligomers terminated with sulfonate [PEO_m–$(SO_3M)_2$] were prepared from PEO oligomers with terminal hydroxy groups as shown in Scheme 1, by the procedure described in previous reports.[31,32] First, the terminal —OH groups were brominated, *e.g.* PEO_{600}–Br_2 was prepared by the reaction of PEO with M_W of 600 (PEO_{600}; 96 g, 0.16 mol) and an excess of thionyl bromide ($SOBr_2$; 100 g, 0.48 mol) in the presence of triethylamine (TEA; 85 ml, 0.6 mol) in toluene (1000 ml). After purification, PEO_{600}–Br_2 (yield: 67 g, 57%) was obtained as a brown liquid. The terminal bromo group was then substituted by a sodium sulfonate group, and the sodium ion was exchanged with the desired alkali-metal cation *via* the sulfonic acid form. For example, PEO_{600}–Br_2 (23.1 g, 3.17 mmol) was dissolved in ethanol (20 ml) and added to an aqueous solution (200 ml) of sodium sulfonate (9.0 g). After refluxing this solution for 3 days, the brownish solution turned yellow suggesting the formation of PEO_{600}–$(SO_3Na)_2$. The solution was then filtered and evaporated at 85 °C for 4 h. Then the residue was dissolved in distilled chloroform (150 ml), cooled to 4 °C and filtered to remove NaBr and Na_2SO_3. The solution was then evaporated at 60 °C and dissolved again in chloroform and refiltered. In order to remove inorganic salts as much as possible, such filtration steps should be carried out at least three times. The amount of chloroform required to dissolve the residue gradually decreased to 50 ml. PEO_{600}–$(SO_3Na)_2$ (yield: 19.3 g, 78.6%) which was obtained as a yellowish wax was carefully added to an excess of hydrochloric acid (1.0 M, 250 ml) to convert the sodium salt into the acid. The solution was evaporated to remove both water and HCl, and then the residue was dissolved in chloroform (100 ml) to enable removal of NaCl. After filtration twice, PEO_m–$(SO_3H)_2$ (12.15 g, yield 66.7%) was obtained. In these preparation steps, inorganic salts such as NaBr, Na_2SO_3 and NaCl could be present. However, no contamination of these impurities was detected by flame tests for each PEO_m–$(SO_3H)_2$ prior to neutralization with alkali-metal hydroxides (MOH; M = Li, Na, K, Rb or Cs) in water to prepare corresponding alkali-metal salts of PEO–sulfonate [PEO_{600}–$(SO_3M)_2$]. The reacted solutions were evaporated for 6 h at 90 °C and then dried under vacuum at 65 °C for 3 days. A series of PEO_m–$(SO_3M)_2$ samples were prepared in a similar manner.



Scheme 1

PEO oligomers containing a sulfonate group at only one end, α-methoxy-ω-alkali metal sulfonate–PEO oligomers, were also prepared by the same method as above using monomethyl ether PEO oligomers with molecular masses of 150, 350, 550, 750 and 2000 as starting materials. The structures of the obtained compounds were confirmed by ^1H NMR spectroscopy.

Methods

^1H NMR spectroscopy in $CDCl_3$ on a JEOL LA-300 (300 MHz) instrument was used to confirm the structure of our hybrids with $SiMe_4$ as an internal reference. DSC measurements were carried out on a DSC-120 (Seiko Instruments Inc.) with a heating rate of 10 °C min^{-1} in the temperature range −120 to 200 °C. The ionic conductivity of PEO_m–$(SO_3M)_2$ and PEO_m–SO_3M samples was measured by the complex impedance method using an impedance analyser (Solartron model 1260; Schlumberger). The dynamic ionic conductivity measurement system which was developed in our laboratory, was used to construct the Arrhenius plot of the ionic conductivity from 6 to 60 °C.[33] The preparation of the sample cell and all the measurements were carried out in a glove-box filled with dry nitrogen gas.

The measurement of transport number was carried out by the complex impedance method and by the direct current polarization method.[34] The sample cell has two lithium electrodes and the applied voltage (ΔV) was 10 mV using a potentiogalvanostat (Nikko Keisoku-NPGS-2501) for direct current polarization. The complex impedance measurement was also carried out with the same apparatus as the ionic conductivity measurement, as described previously.[33] The measurement of transport number was carried out under argon flow in a glove-box. The transport number was calculated by the steady current [$I(\infty)$], obtained by direct current polarization, and the bulk and charge transfer resistance (R_b and R_e, respectively) using the equation;

$$t_{Li^+} = R_b / \{\Delta V / I(\infty) - R_e\} \qquad (1)$$

Results and Discussion

Each step in the preparation of PEO–$(SO_3M)_n$ ($n = 1$ or 2) from PEO or PEOM was monitored by ^1H NMR spectroscopy. When the terminal —OH groups were brominated, the protons of the nearest methylene groups (*b* and *c* in Scheme 1) gave triplets at δ 3.47 and 3.81, respectively as shown in Fig. 1(A). The integrated signal intensity ratio, *a*:*b* or *a*:*c*, was in accord with the number of oxyethylene (OE) units in each sample. When the terminal group was —SO_3Na after reflux of PEO–Br_2 with $NaSO_3$, the proton signals for *b*′

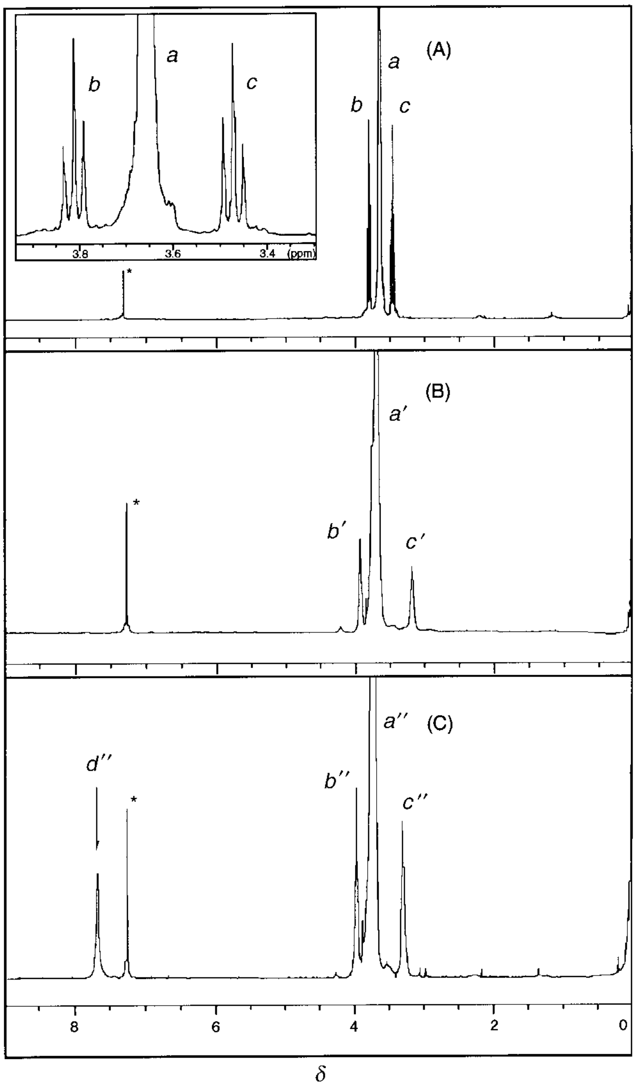


Fig. 1 ^1H NMR ($CDCl_3$, $SiMe_4$) spectra for terminal replaced PEO oligomers at 20 °C. (A) PEO_{600}–Br_2, (B) PEO_{600}–$(SO_3Na)_2$, (C) PEO_{600}–$(SO_3H)_2$; * $CHCl_3$.

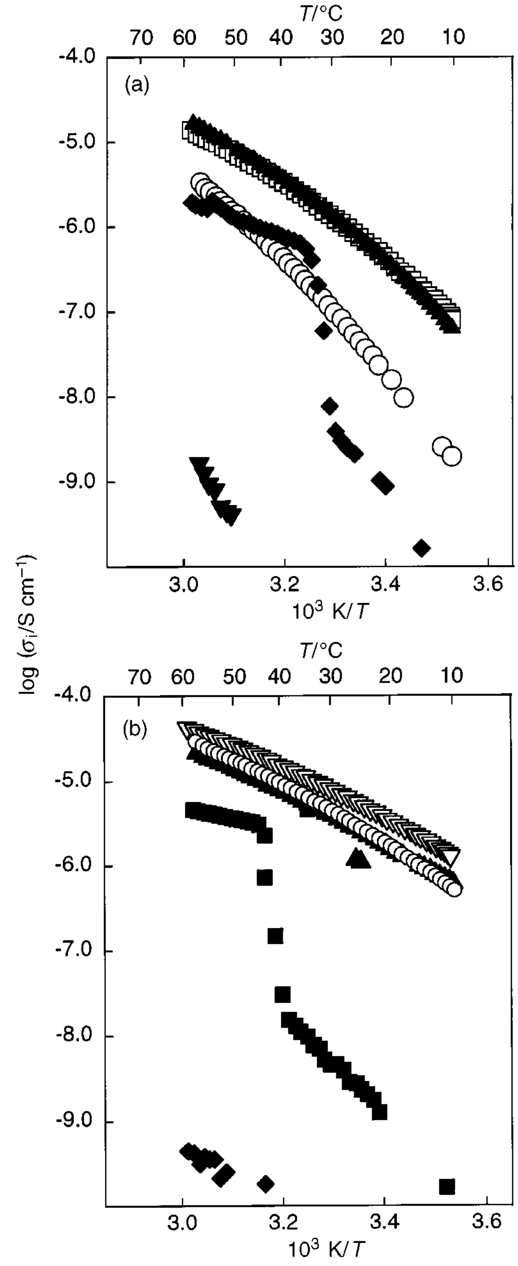


Fig. 2 Temperature dependence of ionic conductivity for (a) PEO_m–$(SO_3Li)_2$ with PEO $M_r = 200$ (▼), 400 (○), 600 (▲), 1000 (□) and 2000 (◆), and for (b) PEO_m–SO_3Li with PEO $M_r = 150$ (◆), 350 (▽), 550 (▲), 750 (○) and 2000 (●)

and c' were at δ 3.17 and 3.92, respectively [Fig. 1(B)] and no peaks were observed at δ 3.47 and 3.81 indicating complete replacement of Br. Upon converting the sodium sulfonate to sulfonic acid groups, the peak (d'') for the sulfonic acid proton was observed at δ 7.70 (d'') [Fig. 1(C)] and vanished after neutralization with MOH. The basic structure, namely, the number of OE units in the PEO part, was also confirmed by the integration ratio of the proton peaks. Since this ratio remained constant, no breakdown of the polyether chains occurred during the reaction.

The temperature dependences of ionic conductivities for PEO_m–$(SO_3Li)_2$ and PEO_m–SO_3Li are shown in Fig. 2(a) and (b), respectively. In both systems, a relatively high lithium ionic conductivity of *ca.* 10^{-5} S cm^{-1} at room temperature was observed in the bulk and is the highest value among α,ω-dicharged PEO oligomers ever prepared. In the PEO_m–$(SO_3Li)_2$ system, the highest ionic conductivity was observed for $m = 600$ and 1000. For derivatives with lower molecular mass, *i.e.*, $m = 200$ and 400, a glass-like phase was observed. Comparing the ionic conductivity of PEO_m–$(SO_3Li)_i$ ($i = 1$ or 2) in the optimum molecular mass range, the highest ionic conductivity was observed for PEO_m–SO_3Li ($m = 350$ and 550). Since these matrices had fairly low molecular mass PEO they can be regarded as single-ion conductors. The lithium transport number (t_{Li^+}) was measured by direct current polarization and, for example, PEO_{350}–SO_3Li had a lithium transport number of *ca.* 0.73–0.81 at 20 °C. The ionic conductivity was confirmed to be derived mainly from cation transport even for a low molecular mass PEO–sulfonate.

On the other hand, the ionic conductivity for both types of matrices with molecular mass for PEO of 2000 showed a drastic temperature dependence attributed to crystallization of the PEO as discussed previously for other derivatives.[20,21] Only high molecular mass PEO–sulfonates such as PEO_{2000}–$(SO_3Li)_2$ and PEO_{2000}–SO_3Li showed a melting point, as confirmed by DSC measurements. To confirm phase transitions of these derivatives, DSC curves of a series of PEO_m–$(SO_3Li)_2$ were recorded and are shown in Fig. 3. PEO_m–$(SO_3Li)_2$ with a PEO molecular mass lower than 1000 showed no thermal response except for a glass transition, and accordingly they were confirmed to be amorphous between −120 and 160 °C. In PEO_{1000}–$(SO_3Li)_2$, the crystallization was prevented upon replacement of terminal hydroxy groups by sulfonate groups, similarly to other PEO/salt hybrids.[27] In

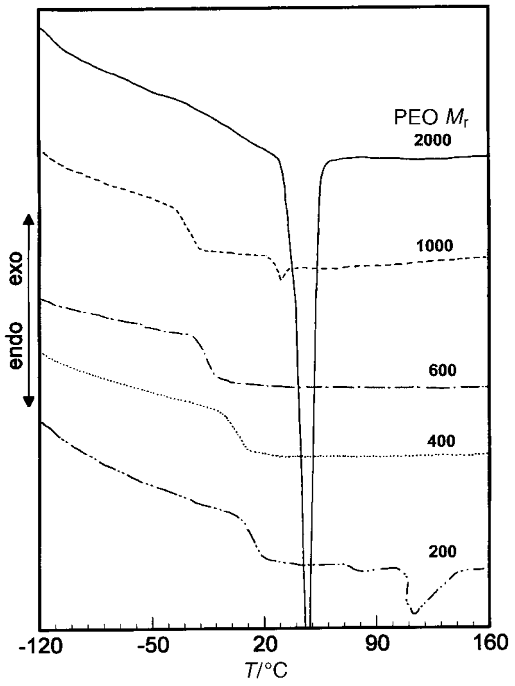


Fig. 3 DSC curves for PEO$_m$–(SO$_3$Li)$_2$. Scan rate + 10 °C min^{-1}.

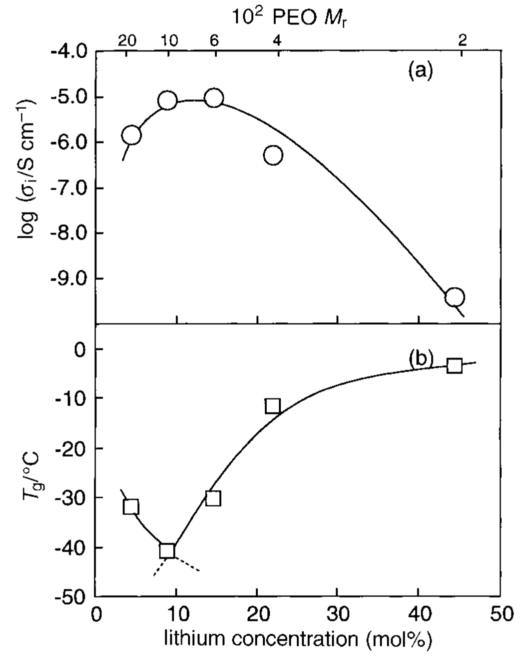


Fig. 4 Effect of the cation concentration on the ionic conductivity at 50 °C (a) and glass transition temperature (b) of PEO$_m$–(SO$_3$Li)$_2$

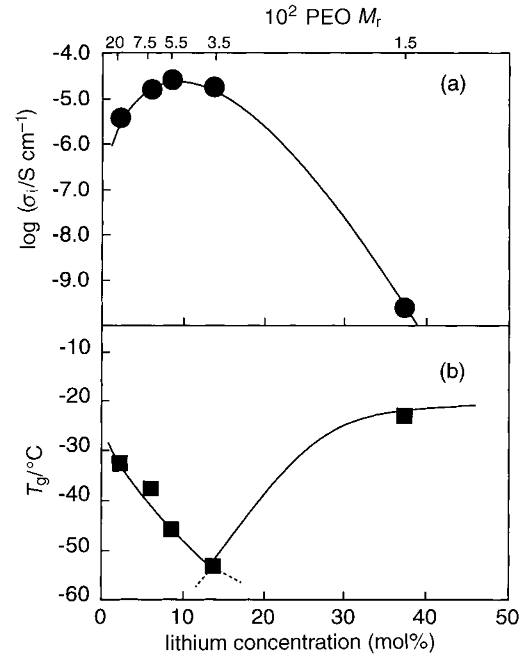


Fig. 5 Effect of the cation concentration on the ionic conductivity at 50 °C (a) and glass transition temperature (b) of PEO$_m$–SO$_3$Li

PEO$_{2000}$–(SO$_3$Li)$_2$, clear thermal peaks arising from crystallization of the PEO were found and the melting point was determined to be 41.3 °C. The melting point of the matrix corresponded to the temperature at which the ionic conductivity dropped as shown in Fig. 2(a). Since ion migration mainly occurs in the amorphous phase, the decrease of ionic conductivity is derived from a decrease of the ion-conductive path. On the other hand, PEO–sulfonates with PEO molecular masses of *ca.* 1000 showed relatively high ionic conductivity and less temperature dependence because they showed an amorphous phase over a wide temperature range. However, PEO$_{2000}$–(SO$_3$Li)$_2$ and PEO$_{150}$–SO$_3$Li showed poor ionic conductivity despite the higher cation concentration and their amorphous nature. In general, the ionic conductivity is known to be governed mainly by the number of carrier ions and their mobility. The number of carrier ions is a function of both the dissociation constant of the terminal groups and their concentration. The cation concentration is a function of the molecular mass of the PEO. Since PEO oligomers having relatively high molecular mass such as 2000 contained only a small amount of carrier ions in the bulk, the ionic conductivity was not high even above the melting point. Upon increasing the cation concentration (decreasing the molecular mass of the PEO), the PEO–sulfonate became stiff and showed a salt-like phase and the mobility of cations decreased considerably.

In order to analyse the effects of ion mobility on the conductivity, the ionic conductivity for PEO$_m$–(SO$_3$Li)$_n$ ($n = 1$ or 2) was analysed together with T_g as a function of cation concentration. These results are summarized in Fig. 4 and 5. The ionic conductivity of PEO$_m$–(SO$_3$Li)$_2$ and PEO$_m$–SO$_3$Li showed maximum values at a cation concentration of *ca.* 10 mol% per OE unit in both matrices. The ionic conductivity was also related with changes of T_g for both types of matrix. Upon increasing the cation concentration, T_g initially decreased to reach a minimum value and then increased at higher concentrations as shown in Fig. 4(b) and 5(b). At a cation concentration < 10 mol% T_g was below -30 °C. Since the dissociation of salts does not induce an increase of T_g in this concentration range, the increased ionic conductivity was attributed to an increase of the number of carrier ions. However, T_g of these matrices started to increase when the cation concentration was > 15 mol%. A similar increase of T_g at higher cation concentration was also observed for PEO oligomers terminated with benzenesulfonate.[27] In PEO–benzenesulfonate, an increase of T_g was observed from 5–7% cation concentration; it is therefore apparent that the absence of an aromatic group is effective in lowering T_g and leads to higher ionic conductivity at higher cation concentrations. Angell *et al.* reported that low molecular mass PEO–sulfonate had high T_g values.[30] Such an increase of T_g might be caused by the high concentration of cations in the matrix. Dissociated ions are known to cause pseudo-cross-linking of PEO chains through ion–dipole interactions between the cations and ether oxygens as frequently observed in PEO derivatives containing inorganic salts. However if the increase of T_g was only a consequence of charge concentration, then compounds with the same cation content should have the same T_g. Comparing

Fig. 4(b) and 5(b), PEO_m–SO_3Li showed 10–20 °C lower T_g values than PEO_m–$(SO_3Li)_2$ at the same cation concentration. For example, PEO_{350}–SO_3Li and PEO_{600}–$(SO_3Li)_2$ showed T_g at −52.8 °C and −30.1 °C at cation concentrations of 13.8 and 15.5%, respectively. While the number of dissociated ions was almost the same in both hybrids, PEO_m–$(SO_3Li)_2$ can construct pseudo-high-molecular mass linear chains through electrostatic interactions of the chain ends and cations might behave as a cross-linking agent for both anionic groups. This effect should also be observed for PEO_m–SO_3M, but here only dimers are formed. This effect also induces an increase of T_g at higher cation concentrations in low molecular mass PEO–sulfonates.

As previously described, one of the advantages of these PEO–sulfonates is their high lithium ion conductivity. To clarify the improved lithium ionic conductivity, the effect of the cation radius on the ionic conductivity in PEO_m–$(SO_3M)_2$ was analysed. The cation radius dependence of the ionic conductivity is small as shown in Fig. 6 and the slope of the obtained relation was identical for a series of PEO_m–SO_3M hybrids. In other PEO/salt hybrids (*e.g.* terminated by carboxylate or benzenesulfonate), the ionic conductivity increased upon increasing the cation radius. Additionally the slope of ionic conductivity *vs.* cation radius in different PEO/salt hybrids decreased upon decreasing the dissociation energy of the terminal group, with sulfonate < benzenesulfonate < carboxylate. This sequence shows a correlation with the estimated dissociation energy of these PEO/salt hybrids in PEO oligomers.[35] Therefore, the slope in Fig. 6 could be explained by the dissociation energy of the terminal group empirically, but the exact physical meaning of the value of these slopes is still obscure. Little cation size dependence in the ionic conductivity is advantageous; an increase of ionic conductivity with increased cation radius could be explained in two ways. One is the difference of the dissociation constant as previously discussed, and the other is the mobility of the cation itself. Since the sulfonate group is a weak conjugate base (*cf.* carboxylate and benzenesulfonate), it is expected to be effectively dissociated even for lithium. In PEO–sulfonate, the degree of dissociation is high and independent of M_w of the PEO. Since the interaction between the cation and ether oxygen increases upon increasing the surface charge density of the cation, smaller cations are strongly suggested to be immobilized onto ether oxygens *via* strong interactions. Since larger cations interact more weakly they are more mobile. Therefore, larger cations show higher ionic conductivity in the PEO–sulfonate systems. Although control of ion–dipole interactions could not be carried out, the influence on the dissociation constant was minimized by the use of sulfonate and led to the improvement of lithium ionic conductivity in PEO–sulfonates.

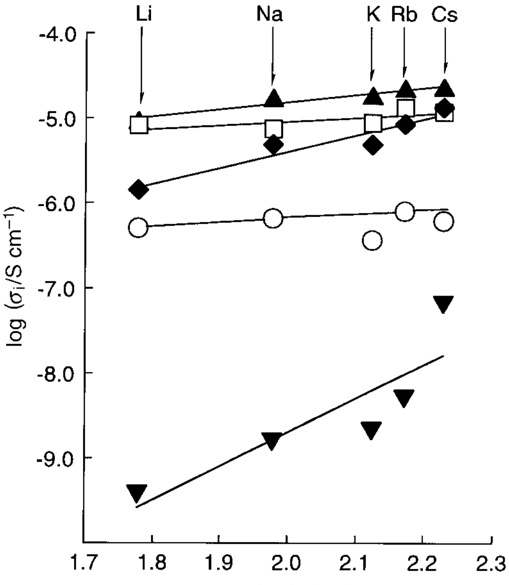


Fig. 6 Effect of cation radius on the ionic conductivity for PEO_m–$(SO_3M)_2$ at 50 °C. $m = 200$ (▼), 400 (○), 600 (▲), 1000 (□) and 2000 (◆).

Conclusion

PEO oligomers containing terminal sulfonate groups have been prepared and their bulk ionic conductivity analysed. An amorphous matrix was obtained when M_W of the PEO was <2000. A high lithium conductivity was observed in both PEO with sulfonate groups on both ends [*e.g.* PEO_{600}–$(SO_3Li)_2$; $\sigma = 1.43 \times 10^{-6}$ S cm^{-1}, 30 °C] and on one end only [*e.g.* PEO_{350}–SO_3Li; $\sigma_i = 4.45 \times 10^{-6}$ S cm^{-1}, 30 °C]. PEO_{350}–SO_3Li showed a higher lithium conductivity than any other PEO/salt hybrid previously prepared. It was confirmed that the matrices were cationic conductors by analysis of their transport numbers. PEO_m–SO_3Li matrices showed a higher ionic conductivity than PEO_m–$(SO_3Li)_2$ at the same charge density because of lower T_g values while their ionic conductivity showed little dependence on the cation radius.

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