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Poly(ethylene oxide)s having carboxylate groups on the chain end

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Poly(ethylene oxide)α,ω-dicarboxylic acid alkali metal salts were prepared as inherently ion-conductive salts. Since the average molecular weight of the poly(ethylene oxide) matrix is about 300, the salts are totally amorphous and show ionic conductivity of 10^{-4}–10^{-6} S cm^{-1} at 50°C. An upwardly convex curve was seen in the Arrhenius plots of the ionic conductivity, reflecting the diffusion of ions in a viscous matrix. Under the same condition, the salts with larger cation showed higher ionic conductivity. These salts, except lithium salt, were miscible with polyether oligomers at any composition, maintaining the high ionic conductivity.

(Keywords: poly(ethylene oxide); ion conduction; alkali metal cation)

Introduction

Poly(ethylene oxide) (PEO) oligomer and its derivatives have been used as the polymer matrix for fast ion conduction[1-3]. Most ion-conductive polymers are obtained easily only by dissolving inorganic salts in PEO derivatives. In such systems, both cation and anion are mobile. In order to apply ion-conductive polymers to future ionic devices, such as polymer batteries, electrochromic displays and so on, a single-ion (mostly cation) conductor is more favourable. Some single-ion conductive polymers have been prepared and their ion conduction behaviour analysed[4-7]. Although the ionic conductivity was improved to show a small time dependence, the ionic conductivity itself was lower than that for an ordinary bi-ion conductor[8]. This was attributed to the reduction of ion mobility and/or decrease of the number of carrier ions. The insufficient conductivity prevented the practical application of ion-conductive polymers. Many attempts have been made to overcome these problems. For example, the synthesis of a new polymer matrix which provides greater mobility of ions[9-11], and the preparation of new salts which have lower dissociation energy thus expecting a higher dissociation degree[12-14]. To increase the number of carrier ions, a large amount of inorganic salt was mixed with a small amount of polyether[15]. To realize higher cation mobility and a greater number of effective carrier ions, we propose here a new type of organic salt which is easily prepared without any problematic steps.

Experimental

Poly(ethylene oxide)α,ω-dicarboxylic acid ($HOOCCH_2O$-$(CH_2CH_2O)_7CH_2COOH$) with molecular weight of about 400 ($PEOA_2H_2$) was neutralized in equimolar proportion with a series of alkali metal hydroxides (MOH; M = Li, Na, K, Rb and Cs) in methanol or water. $PEOA_2H_2$, purchased from Kawaken Fine Chemical Co. Ltd, was neutralized, and the obtained solution was treated with 5 wt% active carbon in water. After filtration, $PEOA_2M_2$ solutions were evaporated at 80°C for 4 h to remove most of the water and methanol. After evaporation, chloroform was added to the residual viscous liquid to expel water molecules as an azeotrope. This solution was refluxed and evaporated again at 80°C for 4 h and dried *in vacuo* at 65°C for 2 days.

PEO with an average molecular weight of 300 (PEO_{300}) was obtained from NOF Ltd, and was dried *in vacuo* before use.

The ionic conductivity of the $PEOA_2M_2$ was measured by a dynamic a.c. impedance analysing system[16] from 10 to 60°C. The frequency was changed from 100 Hz to 1.0 MHz to draw the Cole–Cole plot.

An X-ray diffraction pattern was obtained by a Rigaku Rad C X-ray diffractometer.

D.s.c. analysis was carried out with a Rigaku-CN80591 thermal analyser. The scanning rate was set at 10 K min^{-1}.

Results and discussion

All the $PEOA_2M_2$ samples were confirmed to be amorphous from −100 to 100°C by d.s.c. measurement. There was only a slight thermal response attributed to the glass transition. X-ray diffraction measurements gave no intensive signals attributed to the crystalline phase.

The temperature dependence of ionic conductivity for $PEOA_2M_2$ is shown in *Figure 1*. All the salts, except lithium salt, showed inherently high ionic conductivity. The ionic conductivity was increased by increasing the cation radius. The lattice energy of these alkali metal salts is known to be decreased with increasing cation radius[3]. The lithium salts dissociate less than other salts, resulting in poor ionic conductivity. Furthermore, smaller cations interacted more strongly with ether oxygens in polyethers because of the larger surface charge density[5,17]. Thus, the mobility was also decreased by decreasing the cation radius[18]. The results of both the lower dissociation degree and slower ion migration are clearly seen as very poor lithium ionic conductivity in *Figure 1*. A caesium salt showed the highest ionic conductivity, 1.5×10^{-4} S cm^{-1} at 50°C. This is an excellent value for a pure organic salt. This value is almost

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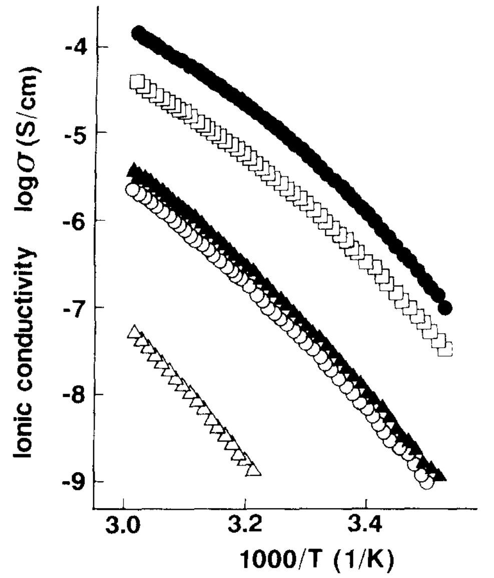

Figure 1 Temperature dependence of ionic conductivity of $PEOA_2M_2$ in the bulk: $M^+ = Li^+$ (△); Na^+ (○); K^+ (▲); Rb^+ (□); Cs^+ (●)

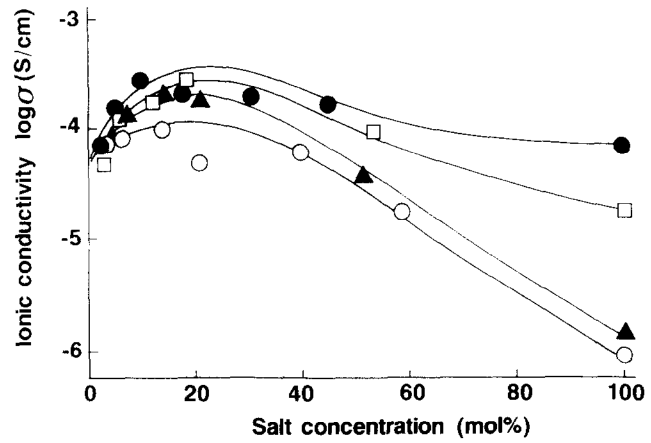

Figure 2 Ionic conductivity of $PEOA_2M_2/PEO_{300}$ mixture at 50°C: $M^+ = Na^+$ (○); K^+ (▲); Rb^+ (□); Cs^+ (●)

equivalent to those for the PEO derivatives containing salts. The Arrhenius plots of the ionic conductivity for all $PEOA_2M_2$ samples were convex curves, i.e. non-Arrhenius behaviour. This is a typical tendency for the ion conduction in polyether derivatives[1-3]. This strongly suggests that the carrier ions were transferred with the segmental motion of PEO chains.

The affinity of salts with PEO structure is an important factor for a supporting electrolyte of a solid state ion conductor, since most solid polymer electrolytes are composed of salts and PEO derivatives. A series of $PEOA_2M_2$ was mixed with PEO oligomers. Since $PEOA_2M_2$ had seven oxyethylene units on average, PEO_{300} was used as a polymer solvent having the same number of oxyethylene unit. A certain amount of $PEOA_2M_2$ and PEO_{300} were mixed well in chloroform, and evaporated at 80°C for 4 h and dried *in vacuo* at 65°C for 2 days. Lithium salt ($PEOA_2Li_2$) was relatively rigid and insoluble in the PEO oligomers. All other $PEOA_2M_2$ samples were soluble in PEO_{300} at any composition, and their ionic conductivity is summarized in *Figure 2*. The caesium salt (20 mol% to PEO_{300}) showed the highest ionic conductivity: 2.7×10^{-4} S cm at 50°C. This high ionic conductivity was retained at even higher salt concentration (>50 mol%). In other systems, the $PEOA_2M_2/PEO_{300}$ mixture showed 4 100 times higher ionic conductivity than those of the corresponding pure $PEOA_2M_2$ salts.

The terminal hydroxyl groups were necessary to dissolve and to dissociate some inorganic salts in polyethers[19,20]. In particular, carboxylic acid salts require a considerable amount of the terminal hydroxyl groups to dissociate[21]. Since $PEOA_2M_2$ has no terminal hydroxyl group, the dissociation of salts was restrained. When these salts were dissolved in PEO_{300}, the dissociation of $PEOA_2M_2$ was enhanced by the terminal hydroxyl groups of PEO_{300}. Higher ionic conductivity was realized by mixing this $PEOA_2M_2$ with PEO oligomers through the improved dissociation degree.

In general, ionic conductivity varied as a function of salt concentration, and showed a maximum value. Namely, the ionic conductivity decreased at higher salt concentration because of a drastic decrease of ion mobility, which was attributable to the interchain crosslinking with cations. On the other hand, the $PEOA_2M_2$ was inherently ion conductive; high ionic conductivity was maintained at higher concentration, even in bulk. It is noteworthy that there is only a slight decrease of ionic conductivity at even higher salt concentration.

Recently, many inorganic salts in polyethers were revealed to be phase-separated to a considerable extent at higher temperature[22-24]. This phase separation should be a considerable drawback for ion-conductive polymers based on the polyether structure, as well as the limited salt solubility. Since $PEOA_2M_2$ (except lithium salt) showed no phase separation even at high temperature because of excellent affinity with PEO oligomers, $PEOA_2M_2$ is considered to have potential use for PEO-related solid electrolytes.

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