

Preparation and ionic conductivity of poly(oligo(oxypropylene) methacrylate)

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Poly(oligo oxypropylene) methacrylate (P(MPO)) was prepared, and a series of alkali metal perchlorates (MClO_4 ; $\text{M} = \text{Li, Na, K, Rb and Cs}$) was dissolved in it to measure ionic conductivity. The lithium ionic conductivity was $\sim 10^{-6} \text{ S cm}^{-1}$ at 303K, and the conductivity decreased monotonously with increasing radius of the alkali metal cation. This tendency was totally the inverse to that observed for the poly(ethylene oxide) derivatives. As the solubility of LiClO_4 was higher than for other perchlorate salts, various lithium salts were dissolved to investigate the effect of the anion on ionic conductivity. The ionic conductivity decreased with increasing lattice energy of the salts. Arrhenius plots of ionic conductivity and glass transition temperature measurements indicated that ionic conductivity was mainly governed by the solubility of the salt in P(MPO). The dissociation energy of the salt is important for ionic conductivity when salts with higher solubility in PPO were used. In a poly(propylene oxide) derivative, the solubility of the salts was concluded to be the most important factor for ionic conductivity.

(Keywords: ion conduction; poly(propylene oxide); ion size)

INTRODUCTION

Ion conductive polymers are expected to be used as substitutes for electrolytic solutions in ionic devices. This would lead to ionic devices being smaller, lighter and more widely applicable. Over 800 papers have been published on ion conductive polymers since they were first reported by Wright in 1973¹. Most of the studies have aimed to improve ionic conductivity in solid polymers. Poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) are typical polymeric base materials for transporting ions in a solid. Inorganic salts could be dissolved in polymers with the aid of ion-dipole interactions, and the salts were dissociated into ions. In addition, for polymers containing the salt, the glass transition temperature (T_g) was preferred to be low to transport carrier ions along with the segmental motion of the polymer at ambient temperatures. Since a crystalline phase was formed in linear PEO when a certain concentration of salt was dissolved², the ionic conductivity was decreased. Many attempts have been made to prevent the formation of a crystalline phase in PEO-based electrolytes, e.g. comb-shaped polymers having PEO side chains^{3,4}, graft polymers⁵, etc.

On the other hand, PPO has less polarity on the ether oxygen than that of PEO because of the methyl group, while the methyl groups provide an amorphous phase because of their steric hindrance. Faster ion transport was expected in such an amorphous PPO at any temperature. There have been many studies on the preparation of ion conductive polymers containing PPO. The ionic conductivity of linear PPO containing lithium salts was analysed in terms of the Vogel-Tamman-Fulcher (VTF) equation⁶⁻¹⁰. The results strongly suggested that ions

were transported along with the segmental motion of PPO chains. Crosslinked polymers with PPO structure were prepared and the ionic conductivity was measured¹¹⁻¹³. A comb-shaped polymer having PPO side chains was also synthesized, and the relationship between the T_g and ionic conductivity was reported^{14,15}. Random copolymers and block copolymers with PPO and PEO were also studied^{16,17}. All of these attempts were aimed at forming a more amorphous domain in the polymer matrix. The main factors yielding high ionic conductivity were reported to be both the segmental motion of the PPO chain and the number of carrier ions. The general ion conduction mechanism was applied to PPO-based polymers. We have already investigated the relationship between ionic conductivity of PEO derivatives and the radius of carrier ions¹⁸⁻²⁰. In this work, a comb-shaped polymer having short PPO side chains was prepared and various inorganic salts were dissolved in the polymer to investigate the effect of carrier ion size on ionic conductivity.

EXPERIMENTAL

Materials

Oligo(oxypropylene) methacrylate (MPO) was supplied by the NOF Co. Ltd. Before polymerization, the number of propylene oxide repeating units was determined to be 5 from ¹H n.m.r. Poly(oligo oxypropylene) methacrylate (P(MPO)) was prepared by free radical polymerization. Dehydrated methanol was bubbled with dry N₂ to eliminate O₂ before polymerization. MPO was dissolved in methanol to prepare a 0.5 mol l⁻¹ solution. Azobisisobutyronitrile (AIBN, 2 mol%) was added to the monomer as a radical initiator. This mixture was stirred at 328K under N₂ for 6h. The solution after polymerization

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was concentrated using an evaporator and dehydrated chloroform solution was added. The polymer solution was poured into a large excess of hexane. Precipitates were filtered, washed with distilled hexane and dried *in vacuo* for 2 days. Unreacted monomer (MPO) in the solid sample was not detected with i.r. spectroscopy.

The copolymer of MPO and methyl methacrylate (MMA), P(MPO-*co*-MMA) (MPO:MMA = 7:3 mol:mol) was donated by NOF Co. Ltd. This was then used after vacuum drying for 2 days.

Reagent grade perchlorate salts (MClO₄; M = Li, Na and K) were purchased from Kanto Chem. Co. Ltd, and were used after drying for 2 days *in vacuo*. RbClO₄ and CsClO₄ were prepared by the neutralization of the corresponding hydroxide (MOH) with perchloric acid (HClO₄) in an aqueous medium at 273K. The reaction mixture was precipitated in excess acetone, collected on a glass filter and dried for 3 days *in vacuo*.

Both P(MPO-*co*-MMA) and P(MPO) were highly viscous and sticky polymers. Polymers and salts were dissolved in distilled methanol and were mixed homogeneously. Then, the mixed solution was cast onto a Teflon plate and dried for 2 days *in vacuo*. All samples were handled immediately in a glove box filled with dry N₂.

Methods

Ionic conductivity was measured with an impedance analyser (Solartron model 1260; Schlumberger). The frequency range used was from 10 Hz to 10 MHz. As the samples were highly viscous, they were sandwiched using stainless steel electrodes with an O-ring type spacer (6 mm diameter, 1 mm thick) to fix the area and the distance between the electrodes. For the dynamic conductivity measurement under rapid heating and cooling, a custom-designed cell, which was developed in our laboratory²¹, was used. The cell was held between two semiconductor heat pump plates, and the scanning (heating or cooling) was confirmed to be stable up to a scanning rate of 10 K min⁻¹. The temperature was monitored by a thermocouple in a sample cell. Rapid heating and cooling was controlled by a computer. The temperature range was set from 280 to 338K. There was no structural change of the samples in this temperature range. The impedance data at every degree were stored on a floppy disk, and the data were analysed to obtain the Arrhenius plots.

A differential scanning calorimeter (Rigaku-CN80591) was used to measure the *T*_g of the samples. The temperature range was set from 120 to 360K, and the thermal response was analysed with a scanning rate of 10 K min⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between salt concentration and ionic conductivity at 303K for P(MPO) containing MClO₄ (M = Li, Na, K, Rb and Cs). P(MPO)/LiClO₄ had the highest conductivity (1.01×10^{-6} S cm⁻¹) when the salt concentration was 4.0 mol% with respect to the OP unit at 303K. This value was the same as that in published conductivity data for polymers having PPO structures⁷. Salts with larger cations gave lower ionic conductivity in P(MPO). The effect of cation species on ionic conductivity was considerably different from that for the PEO derivatives. Generally, higher conductivity was observed for PEO derivatives containing larger alkali

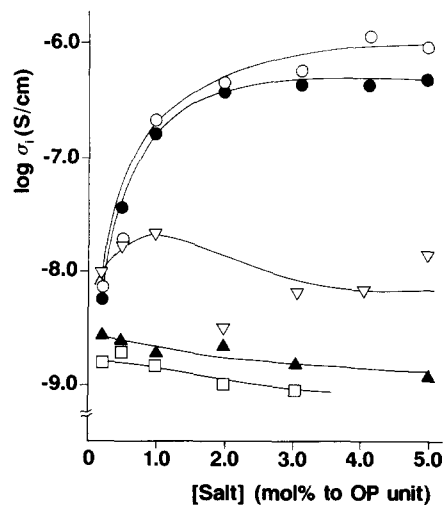


Figure 1 Ionic conductivity for P(MPO) containing MClO₄ at 303K. M: (○) Li; (●) Na; (▽) K; (▲) Rb; (□) Cs

metal cations because of weaker ion-dipole interaction (i.e. larger mobility). It is known that the polarity of PPO was less than that of PEO. PPO could dissolve the salts without forming a crystalline phase because of the steric hindrance of the methyl groups. The PPO unit in P(MPO) was considered to show a smaller contribution to solubilize the salt than the PEO unit. The solubility of the salt decreased with increasing cation radius in the salt. The salt with a larger cation could be dissociated less in P(MPO). The ionic conductivity (σ) was described by the following expression:

$$\sigma = ne\mu \quad (1)$$

where n is the number of carrier ions, e is the elementary electric charge and μ is the mobility of the carrier ion, respectively. The ionic conductivity is therefore governed by both μ and n . It can be said that μ would increase with increasing radius of the alkali metal cations. There is a following tendency that higher ionic conductivity is observed for polymer containing larger alkali metal cations¹⁸. Such a tendency was never observed in the P(MPO)/MClO₄ system. The ionic conductivity for P(MPO)/MClO₄ was suggested to be governed more by n rather than μ .

The *T*_g was measured to evaluate the effect of salt in P(MPO) (Figure 2). The *T*_g of P(MPO) was 221K. The *T*_g was increased when LiClO₄ and NaClO₄ were added. These results indicated that the crosslinking of the PPO side chains was followed by salt dissociation. The effect of salt concentration on the *T*_g of P(MPO) was not observed when RbClO₄ or CsClO₄ was added, as shown in Figure 1. Only a little RbClO₄ and CsClO₄ should be dissociated and most salts were considered not to be dissociated but simply to be dispersed in the polymer.

For further consideration of cation dependence on ionic conductivity, the temperature dependence of ionic conductivity was measured. The results are summarized in Figures 3–7. Figure 3 shows the Arrhenius plot of ionic conductivity for P(MPO) containing 0.2–5.0 mol% LiClO₄. The ionic conductivity of P(MPO) containing 0.2 mol% LiClO₄ was monitored every degree in the temperature range 280–338K. The remaining samples were also analysed. To avoid confusion, the other plots are simply depicted as lines. Figures 4–7 show the temperature dependence of ionic conductivity also as lines for the same reason.

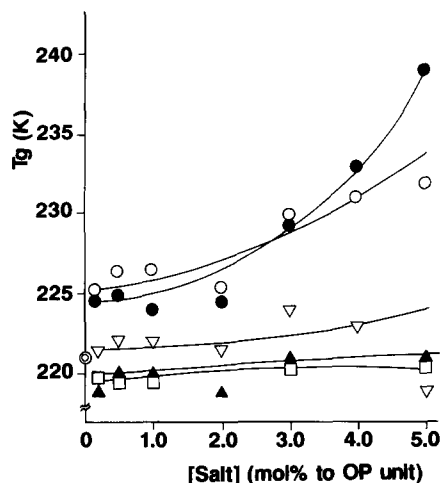


Figure 2 Effect of salt concentration on the glass transition temperature of P(MPO) containing MClO₄. Symbols as in Figure 1; (⊙) without salt

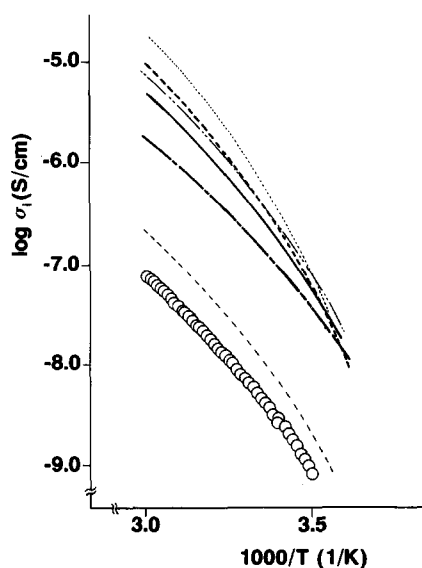


Figure 3 Temperature dependence of ionic conductivity for P(MPO) containing LiClO₄. Salt concentration (mol% to OP unit): (○) 0.2; (---) 0.5; (-·-) 1.0; (—) 2.0; (— — —) 3.0; (- - -) 4.0; (- · · -) 5.0

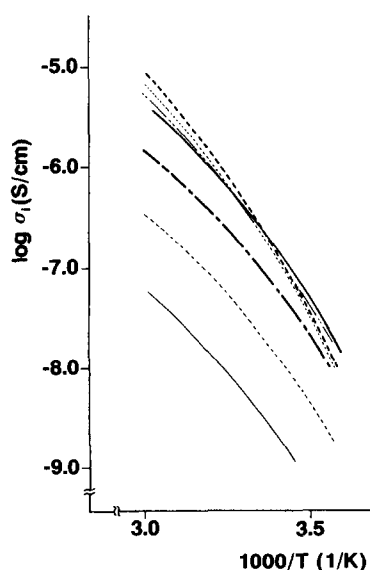


Figure 4 Temperature dependence of ionic conductivity for P(MPO) containing NaClO₄. Symbols as in Figure 3, except: (—) 0.2 mol% to OP unit

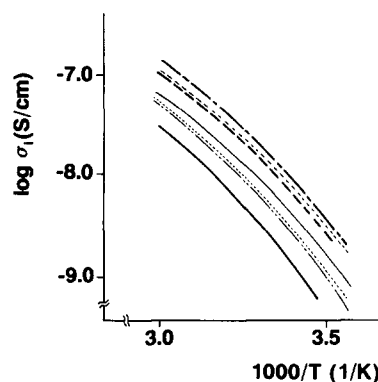


Figure 5 Temperature dependence of ionic conductivity for P(MPO) containing KClO₄. Symbols as in Figure 4

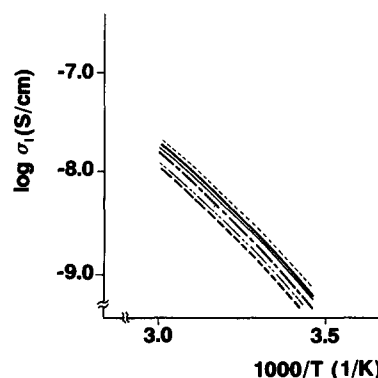


Figure 6 Temperature dependence of ionic conductivity for P(MPO) containing RbClO₄. Symbols as in Figure 4

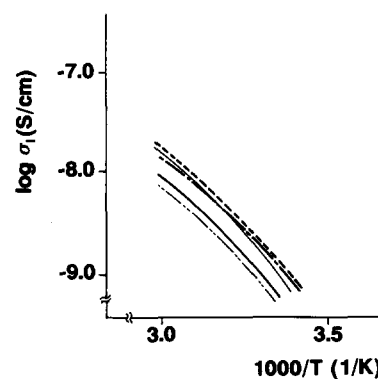


Figure 7 Temperature dependence of ionic conductivity for P(MPO) containing CsClO₄. Symbols as in Figure 4

The Arrhenius plots of ionic conductivity for P(MPO)/LiClO₄ (Figure 3) or P(MPO)/NaClO₄ (Figure 4) show that both the ionic conductivity and the slope of the Arrhenius plots increased with increasing salt content. This indicated that the salts in P(MPO) were dissociated efficiently to increase ionic conductivity and also to induce intermolecular interaction through ion-dipole interactions. The P(MPO)/KClO₄ (Figure 5) plot shows that the ionic conductivity increased up to a salt concentration of 1.0 mol%, but salt concentration dependence was hardly observed. Further, the salt having larger cations, such as RbClO₄ or CsClO₄, showed considerably lower solubility. The Arrhenius plots of ionic conductivity for P(MPO) containing these salts (Figures 6 and 7, respectively) show the extreme case. In P(MPO), these salts (RbClO₄ and CsClO₄) should be dissociated

only a little (perhaps <0.5 mol%). The number of dissociated carrier ions in the polymer should be constant regardless of the salt concentration.

The solubility of the salt eventually governs the ionic conductivity. As the lithium salt showed the highest conductivity among the P(MPO)/MClO₄ systems, the ionic conductivity was analysed for P(MPO) containing a series of lithium salts. Figure 8 shows the effect of lattice energy of lithium salts on ionic conductivity for the corresponding salt-containing P(MPO). The salt with the lowest lattice energy was dissociated more easily in the polymer. This caused an increase in the number of carrier ions, which was important to increase ionic conductivity. Such a tendency is clearly observed in Figure 8. However, the data for P(MPO)/LiNO₃ were eliminated since a value much larger than the expected value was obtained. No reasonable explanation for the data for P(MPO)/LiNO₃ was obtained.

All results indicate that the dominant factor for ionic conductivity for the P(MPO)/salt system was the solubility of the salt. The T_g of all the samples was measured, and the ionic conductivity was analysed with the T_g in terms of the VTF equation:

$$\sigma(T) = AT^{-1/2} \exp[-B/(T - T_0)] \quad (2)$$

where $\sigma(T)$ is the ionic conductivity at T (K), T_0 is the ideal transition temperature, and A and B are constants, respectively.

The ionic conductivity data were fitted on the VTF equation using systems developed in our laboratory. T_0 is known as the temperature where the configurational entropy is zero, and it is simply estimated from the expression²²: $T_g/T_0 = 1.3$. The VTF plots were obtained with T_0 for every sample, which was estimated from the above expression. The obtained ionic conductivity data laid well on the VTF plots. Furthermore, T_0 was determined from a series of calculations where the VTF equation provided a better fitting to all plots. Figures 9 and 10 show the results of data for P(MPO) containing different salts. The cation and anion dependence are shown in Figures 9 and 10, respectively. The slopes of the VTF equation were almost identical. It was confirmed that there was no influence of the salt species on the mobility of the polymer. It was concluded that the ionic conductivity of the P(MPO) system was governed by the

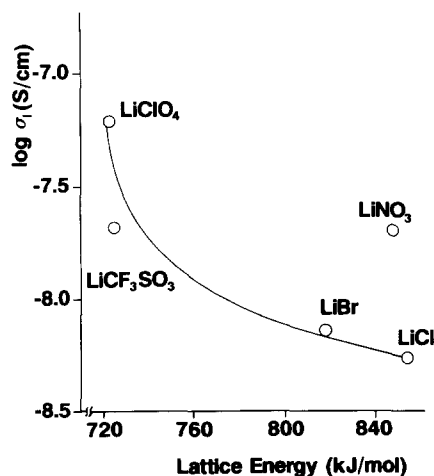


Figure 8 Relationship between the lattice energy of the LiX salt and ionic conductivity of P(MPO) containing LiX at a salt concentration of 1.0 mol% to OP unit at 303K

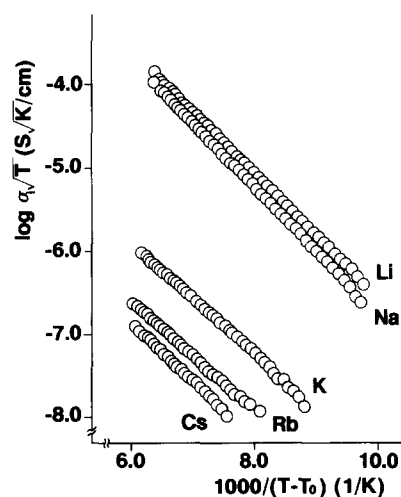


Figure 9 VTF plot for P(MPO) containing MClO₄. [Salt] = 3.0 mol% to OP unit

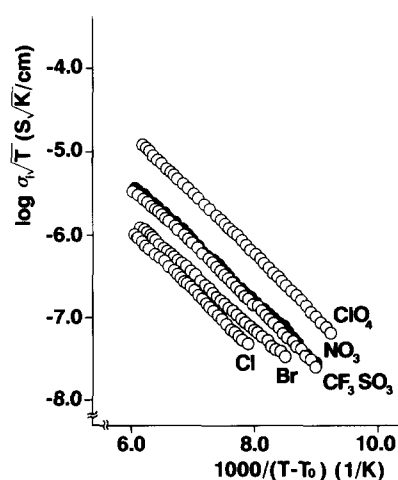


Figure 10 VTF plot for P(MPO) containing LiX. [Salt] = 1.0 mol% to OP unit

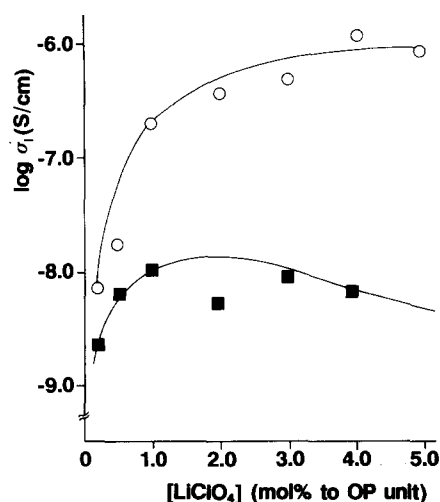


Figure 11 Effect of LiClO₄ concentration on the ionic conductivity for P(MPO-co-MMA) at 303K: (○) P(MPO); (■) P(MPO-co-MMA)

number of carrier ions. The number of carrier ions was a function of the lattice energy and solubility of the salts.

The properties of the polymer films are important for the application of ion conductive polymers in solid devices. As P(MPO)/MClO₄ gave a highly viscous polymer as previously described, the mechanical proper-

ties of the cast films were poor. To improve the mechanical properties of the films, the copolymer of MPO and methyl methacrylate (MMA) was analysed. LiClO_4 was dissolved in P(MPO-co-MMA) and its ionic conductivity was measured (Figure 11). P(MPO-co-MMA)/ LiClO_4 gave a self-standing film by the considerable contribution from MMA. However, the ionic conductivity decreased to 1/100th of that of P(MPO). As the T_g of P(MPO-co-MMA) was higher than that for pure P(MPO), the mobility of the ions should not be sufficient to migrate in the polymer. The copolymerization of MPO and MMA or other monomers could improve the mechanical properties of the cast film, but ionic conductivity was reduced considerably by copolymerization.

CONCLUSIONS

P(MPO) was prepared and then alkali metal perchlorates were dissolved in it. The solubility of salts in P(MPO) was poor, and solubility decreased with increasing cation radius of the added salts. Lithium salts have relatively better solubility. The effect of anion species for a series of lithium salts shows that there was higher ionic conductivity for the system containing the salt with lower lattice energy. It was concluded that the dominant factor for ionic conductivity of P(MPO) was the solubility of salts in P(MPO).

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