Conduction of alkali metal cations in poly(diaza-crown ether)s having hydroxyethyl side arms

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Poly(diaza-3*n*-crown-*n*)s having hydroxyethyl side arms (PDC$_n$s: $n = 5$–7) were prepared, and their effects on the ionic conductivity of both inorganic salts and cation conductive polymers were analysed. A series of alkali metal perchlorates ($MClO_4$: M = Li, Na, K, Rb, and Cs) were mixed with the PDC$_n$ materials. However, although ionic conductivity better than 10^{-6} S cm^{-1} above 60°C was achieved, no effect was seen of any specific coupling of the cation and the crown cavity size on the ionic conductivity. This was probably due to the contribution of the anion conduction. In order to neglect the effect of anion migration, cation conductive polymers were mixed with the PDC$_n$ materials. K^+ and Na^+ showed the lowest ionic conductivity in PDC$_6$ and PDC$_5$, respectively, reflecting stronger interactions with crown ethers having more suitable cavity sizes. The presence of crown ether units in the polymer was also suggested as being responsible for accelerating the dissociation of salts with cations which were smaller than the size of the crown ether cavity.

(Keywords: poly(crown ether); ion conduction; alkali metal ions)

INTRODUCTION

Poly(ethylene oxide) (PEO), a typical ion conductive polymer, can solubilize and dissociate many inorganic salts through ion–dipole interactions. These polymers are potential candidates for the conversion of 'wet' ionic devices into 'dry' systems, when they are used as electrolyte layers[1]. These ion conductive polymers should find wider application if further functions are added to them. For example, ionic conductivity switching devices have been designed by making use of materials which exhibit thermotropic phase transitions[2,3]. The ionic conductivity was also reported to be controlled by irradiation with light[4]. Recognition of the carrier ion species is one of the most interesting functions to be given to ion conductive polymers. On the other hand, crown ether rings are known to show specific recognition of cations[5]. We have preliminarily reported that polymers having the diaza-18-crown-6 unit recognized the K^+ ion in the solid state, resulting in a lower ionic conductivity[6]. It should be noted that any effect of solvation should be absent in ion conductive polymers. However, ions are pseudo-solvated by the ether units of the ion conductive polymers, and they migrate as naked ions by cooperatively forming and breaking the ion–dipole interaction. The effect of the actual cation size may be reflected in the interaction. In this present paper, poly(diaza-crown)s having hydroxyethyl side arms[7] were mixed with cation conductive polymers to evaluate the selective cation conduction in the poly(crown ether)s.

EXPERIMENTAL

Materials

Diaza-15-crown-5, diaza-18-crown-6, and diaza-21-crown-7 were purchased from Aldrich, and recrystallized from heptane before use. A series of polymers, having diaza-3*n*-crown-*n* units with hydroxyethyl side arms (PDC$_n$: $n = 5$–7), were prepared by the reaction of various diaza-crown ether diamine precursors and 1,2:7,8-diepoxyoctane[8]. These polymers were abbreviated as follows: poly[(1,4,10-trioxa-7,13-diazacyclopentadecane-7-13-diyl)(2,7-dihydroxyoctamethylene)] (PDC$_5$), poly[(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7-16-diyl)(2,7-dihydroxyoctamethylene)] (PDC$_6$), and poly [(1,4,10,13,16-pentaoxa-7,19-diazacyclohenicosane-7-19-diyl)(2,7-dihydroxyoctamethylene)] (PDC$_7$). The number-average molecular weights of these PDC$_n$ polymers were estimated to be ~2000–5000 from g.p.c. measurements (elution by THF, calibrated with polystyrene standard samples).

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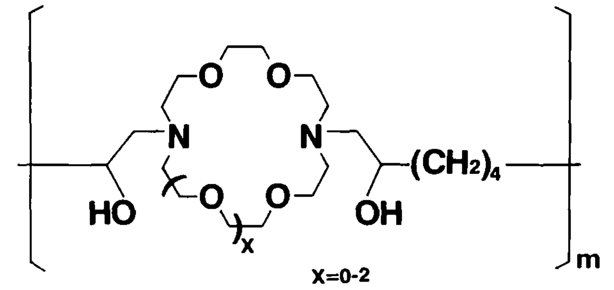

Structure of PDC$_n$

Oligo(oxyethylene) methacrylate (MEO) was purchased from the NOF Company Ltd and was used after drying *in vacuo*. Methacrylic acid alkali metal salts (MAAM: M = Li, Na, K, Rb, or Cs) were prepared by the neutralization of methacrylic acid with the corresponding alkali metal hydroxides in an aqueous medium at 0–5°C[9]. The reaction mixtures obtained were poured into acetone to give needle-like crystals of MAAM. These crystals were then washed, filtered and dried *in vacuo*.

Salt-containing PDC$_n$ Films. PDC$_n$ was dissolved in dry chloroform, and then the required alkali metal perchlorate ($MClO_4$: M = Li, Na, K, Rb, or Cs) was further dissolved in it. The ratio of crown unit structure to metal cation was set to be 20:1. The salt-containing PDC$_n$ film was isolated by evaporating off the chloroform, and was then dried *in vacuo* for 3 days at room temperature.

Copolymerization of MEO and MAAM. MEO and MAAM (MAAM: M = Li, Na, K, Rb, or Cs) were copolymerized in the bulk[9]. MEO, MAAM, and azobisisobutyronitrile (AIBN) were dissolved in distilled methanol. The concentration of MAAM was set to be 2.0 mol% with respect to an oxyethylene unit of the MEO; in other words, the mole ratio of MAAM to MEO was 1:6. The concentration of AIBN was 2.0 mol% with respect to the vinyl monomers. This methanol solution was allowed to evaporate at room temperature in order to remove solvent, and was then heated at 70°C for 3 h to obtain the copolymer of MEO and MAAM (P(MEO-MAAM)). These samples were used after drying *in vacuo*. No vinyl groups were found in the copolymers by using infra-red spectroscopy.

PDC$_n$/P(MEO-MAAM) blends. To prepare a cation conductive polymer blend, PDC$_n$ was simply mixed with P(MEO-MAAM). The two components were individually dissolved in dry chloroform, and the solutions were well mixed and then evaporated to give the PDC$_n$/P(MEO-MAAM) blend film. The ionic conductivities of these films were measured after drying the samples *in vacuo*.

Post-copolymerization of PMEO and MAAM in the presence of PDC$_n$. PDC$_n$ was first dissolved in dry chloroform, and then sufficient MAAM was added to this solution to obtain a mole ratio for the crown ether unit/metal cation of 2:1. After any complex formation of PDC$_n$ with MAAM had taken place, MEO was then added to this chloroform solution ([MEO]:[MAAM] = 6:1). AIBN (2.0 mol% with respect to the vinyl monomers) was added and the system was heated at 70°C for 3 h after evaporating off the chloroform. The solid obtained was further dried *in vacuo* for a period of more than 2 days.

Methods

Ionic conductivity was measured over the temperature range from 10 to 60°C by using a computer controlled Solartron machine (Shulumberger). The dynamic impedance measurement (100 Hz–10 MHz) was carried out using custom-designed apparatus at a heating and cooling rate of 3.0°C min^{-1} (refs 2, 3, 10). The impedance data obtained (recorded on a floppy disk), were analysed to give Cole–Cole plots, and the ionic conductivity was also determined. Preparation of the sample cells and the conductivity measurements were carried out in a glove box filled with dry nitrogen gas.

RESULTS AND DISCUSSION

Bi-ionic conductor: PDC$_n$/$MClO_4$ mixture

The ionic conductivities of various PDC$_n$/$MClO_4$ mixtures were measured and compared in order to evaluate the cation size dependence of the bi-ion conductive systems. *Figure 1* shows the ionic conductivity (σ_i) of various $PDC_6/MClO_4$ mixtures at 55°C. Since the solubility of both $CsClO_4$ and $RbClO_4$ in PDC_6 was relatively poor, the mole ratio of [M^+] to [crown ether unit] was set to be 1:20. As shown in *Figure 1*, the $PDC_6/LiClO_4$ mixture showed a better ionic conductivity than the other systems. It is known, however, that a higher ionic conductivity was obtained for those systems having larger cations[9,11]. The mixtures in this study did not show any such general tendency regarding cation size dependence. Although specific interactions between the PDC_6 crown ether units and K^+ were expected to decrease the conductivity, no such specific effect was detected in this bi-ionic conductor. One of the 'negative' factors here might be the presence of anions.

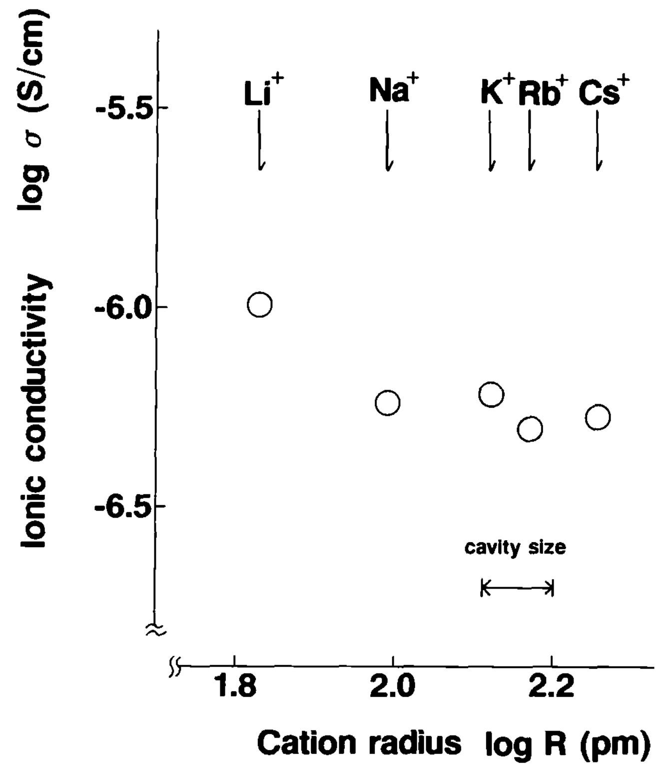

Figure 1 Effect of cation radius on the ionic conductivities of $PDC_6/MClO_4$ mixtures at 55°C. [M^+]:[crown ether unit] = 1:20

It is known that the mobility of anions is generally larger than that of cations in bi-ionic conductors[1], which might conceal the effect of specific interactions between K$^+$ and the diaza-18-crown-6 units.

Single ionic conductor: polymer blend

To cancel out the considerable contribution of the anions to the ionic conductivity, PDC$_6$ was mixed with the cation conductive polymer, P(MEO–MAAM). It has already been reported that P(MEO–MAAM) shows cation (M$^+$) conduction in the region of $\sim 10^{-7}\,\mathrm{S\,cm^{-1}}$. The cationic conductivity was improved by an increasing cation radius[9]. The cation conductive polymer system was prepared by mixing PDC$_n$ and P(MEO–MAAM). However, the polymer blends of PDC$_6$ and P(MEO–MAAM) showed almost the same ionic conductivities as those of the P(MEO–MAAM) system. Cations were surrounded by the oligo(oxyethylene) side chains even after mixing with the PDC$_6$, and might migrate in the conductive domain of the P(MEO–MAAM). No significant effects were found in either of the other polymer blends of P(MEO–MAAM) with PDC$_5$ and PDC$_7$ (data not shown).

In solution, the specific interaction of the metal ion with oligoethers is known to be increased according to the following sequence[12–14]:

linear oligo(ethylene oxide) < crown ether
< diaza-crown ether having side arms < cryptand

This sequence was believed to result from the different stability constants of the various metal ion complexes. In contrast, the completely inverse sequence was found for the rate constants of this complex formation. Consequently, the complex formation of cations with PDC$_n$ should be relatively slow, which might explain the above results. It is suggested that the metal cations in P(MEO–MAAM) were surrounded and stabilized by the linear oligo(ethylene oxide) side chains, and hardly form any complexes at all with the crown units after simple mixing with PDC$_n$.

Single ionic conductor: post-copolymerization system

For discussion of specific interactions between the metal cations and the crown units, it was important to form complexes before the impedance measurements were made. Taking this into account, PDC$_n$ was mixed with MAAM to form complexes in chloroform in advance. To this solution, MEO was added and then copolymerized with the MAAM/PDC$_n$ complex.

Figure 2 shows the Arrhenius plot of the ionic conductivity of PDC$_6$/P(MEO–MAAK) obtained in this way. Conductivity data for P(MEO–MAAK) is also shown in this figure for reference. Both Arrhenius plots are depicted as convex lines, suggesting that the ions are transported by the segmental motion of the polymer chains[1,3]. The ionic conductivities of the PDC$_6$/P(MEO–MAAK) system were lower than those of the P(MEO–MAAK) system at all temperatures. This decrease in the ionic conductivity was believed to be due to complex formation of K$^+$ with the diaza-18-crown-6 unit. The potassium ions are considered to be fixed by the crown ether unit only after the post-copolymerization of MAAM/PDC$_6$ and MEO.

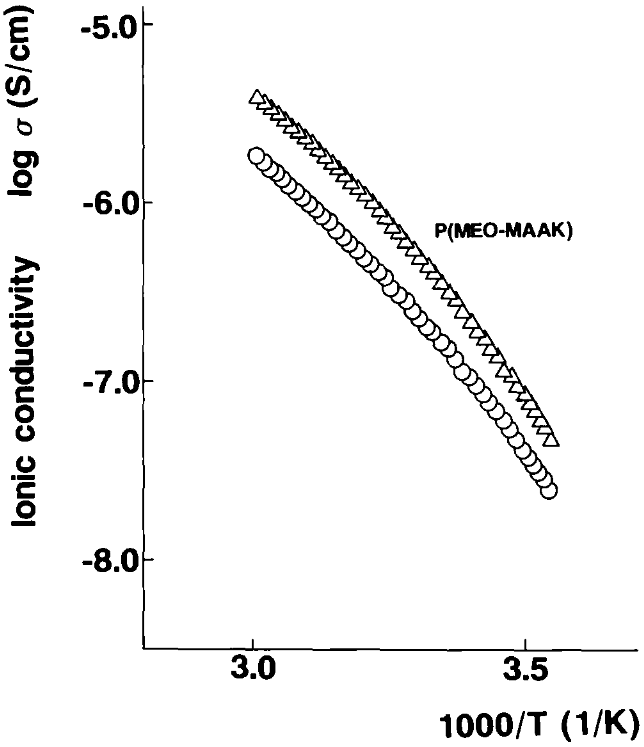

Figure 2 Arrhenius plots of ionic conductivity: (○) PDC$_6$/P(MEO–MAAK) mixture; (△) P(MEO–MAAK). [K$^+$]:[crown ether unit] = 1:2

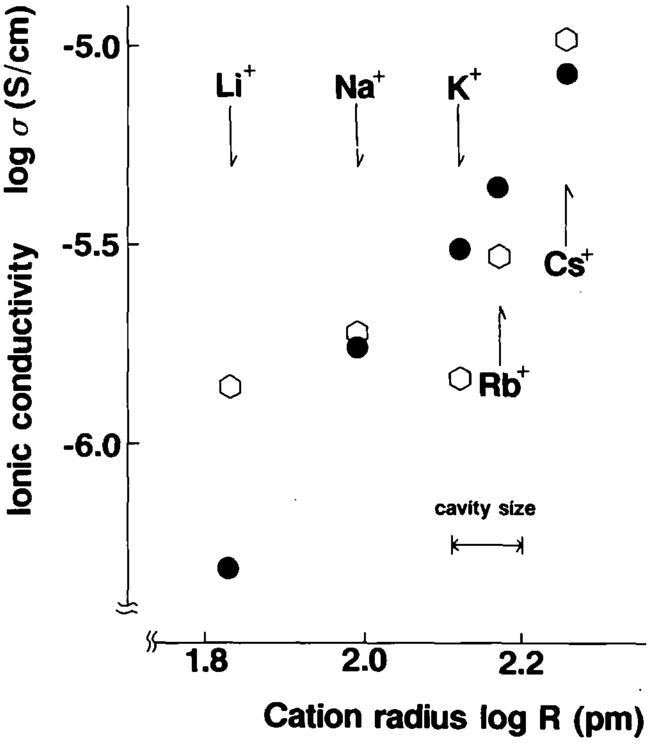

Figure 3 Effect of cation radius on the ionic conductivities measured at 55°C: (○) PDC$_6$/P(MEO–MAAM) mixture; (●) P(MEO–MAAM). [M$^+$]:[crown ether unit] = 1:2

The ionic conductivities of a series of PDC$_6$/P(MEO–MAAM) mixtures were analysed. The effect of the cation radius on the ionic conductivity at 55°C is shown in *Figure 3*. The conductivity data measured at 55°C for a series of P(MEO–MAAM) mixtures were also plotted in this figure for reference. Both of the systems having the

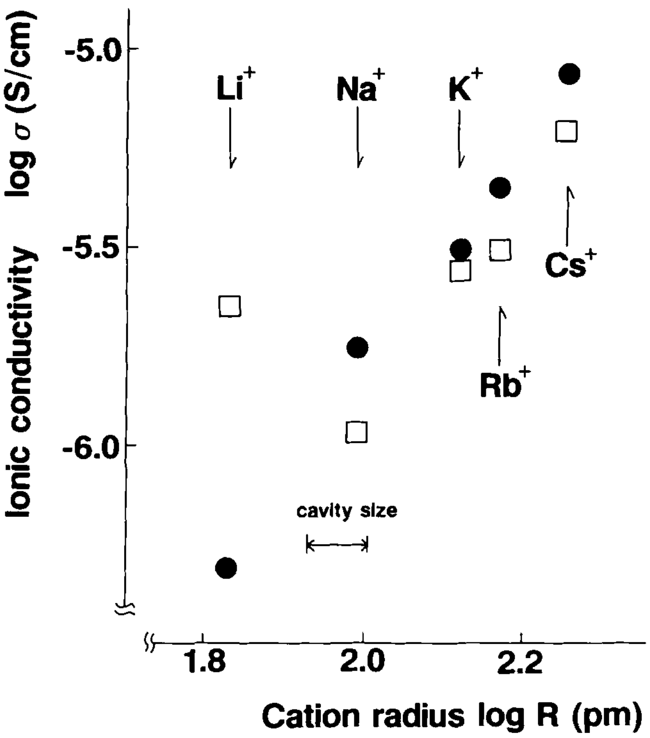

Figure 4 Effect of cation radius on the ionic conductivities measured at 55°C: (□) PDC_5/P(MEO-MAAM) mixture; (●) P(MEO-MAAM). $[M^+]$:[crown ether unit] = 1:2

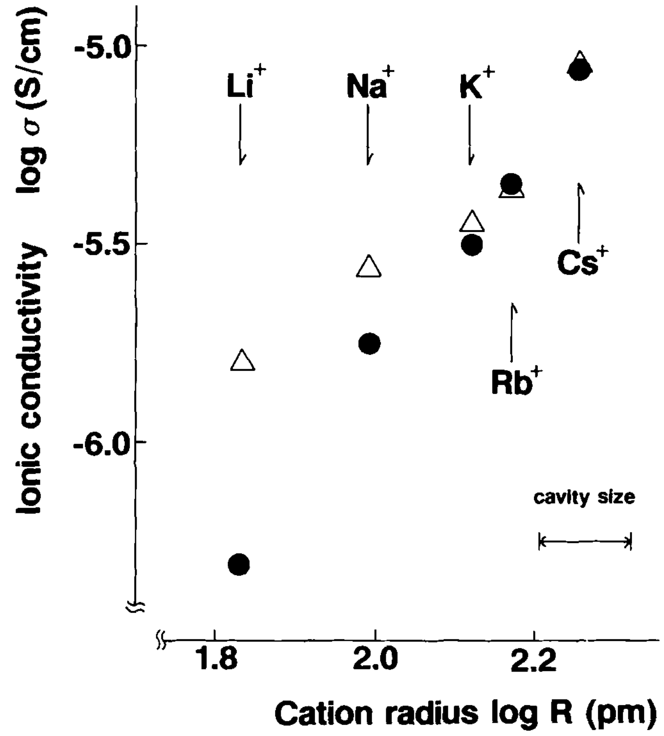

Figure 5 Effect of cation radius on the ionic conductivities measured at 55°C: (△) PDC_7/P(MEO-MAAM) mixture; (●) P(MEO-MAAM). $[M^+]$:[crown ether unit] = 1:2

larger cations showed higher ionic conductivities, as reported previously[9]. This tendency was believed to be due to a weaker ion–dipole interaction force for the larger cations. The ionic conductivities were almost the same for both the PDC_6/P(MEO-MAAM) and P(MEO-MAAM) systems with Na^+ and Cs^+ as the cation. It was remarkable that the ionic conductivities of the systems containing K^+ and Rb^+ were reduced by the presence of PDC_6, as shown in *Figure 3*. It is known that the 18-crown-6 ring shows a stronger complex-forming ability with K^+ than with the other cations. This decrease in the ionic conductivity was considered to originate from the specific complex formation of K^+ with PDC_6. In fact, the 1:1 complex of K^+ and diaza-18-crown-6 containing side arms has already been reported[7,12]. Although the effect was small, a similar restriction of the ion conduction was also found in the Rb^+ system. The cation radius of Rb^+ and the cavity size of the diaza-18-crown-6 unit (marked on *Figure 3*) suggested possible complex formation. Therefore, it was also suggested that Rb^+ might become trapped in the crown cavity of PDC_6 to some extent, thus reducing the ionic conductivity.

In contrast, the ionic conductivity of Li^+ was improved from 4.9×10^{-7} to $1.38 \times 10^{-6}\,S\,cm^{-1}$ (2.8 times) by the presence of PDC_6. Since Li^+ is much smaller than the size of the crown cavity of PDC_6, Li^+ does not form a stable complex with the latter. The polar environment of the PDC_6 is considered to induce the dissociation of the MAALi unit. It was suggested here that crown ether units were effective in inducing the dissociation of salts having smaller cations.

The effect of PDC_5 on the ionic conductivity of P(MEO-MAAM) was also analysed. PDC_5 has a diaza-15-crown-5 ring which exhibits a stronger interaction force with Na^+. The ionic conductivities of a series of PDC_5/P(MEO-MAAM) mixtures at 55°C is shown in *Figure 4*. As expected, the ionic conductivity of P(MEO-MAANa) was reduced by the presence of PDC_5. Since the size of Na^+ fits the cavity of the diaza-15-crown-5 ring, Na^+ ions were trapped in this cavity and a smaller amount of these ions might be transported through the system. Furthermore, the ionic conductivities for both P(MEO-MAARb) and P(MEO-MAACs) were also reduced by the presence of PDC_5. These decreases were explained by the poor compatibility of these salts with PDC_5. Turbid systems, i.e. partly phase-separated samples, were obtained after the post-copolymerization of MEO and MAAM (where M = Rb and Cs) which had been complexed with PDC_5. PDC_5/P(MEO-MAACs) was more turbid than the corresponding Rb system, probably due to the poor compatibility of MAACs and PDC_5. The mixture of MAACs and PDC_5 was obtained as a turbid, viscous solid even before polymerization, thus reflecting poor compatibility. Therefore, the decreases in the ionic conductivities for both of the PDC_5/P(MEO-MAAM) (M = Rb and Cs) systems were attributed to the reduced amounts of effective carrier ions. We have, however, no data on the ionic conductivities for these same systems with lower salt concentrations, because of the limited amounts of PDC_n available.

It was notable that the ionic conductivity of the PDC_5/P(MEO-MAALi) system reached 4.5 times higher than that without PDC_5. Considering such increases in the ionic conductivity for Li^+ ionic conductors in the presence of PDC_n, polymerized crown rings seemed to induce further dissociation of the salts in the solid. Furthermore, Li^+ is only weakly trapped by the crown rings, so the ionic conductivity in the presence of PDC_n was higher than the corresponding P(MEO-MAALi) material. This induction of salt dissociation by the crown rings was previously seen in *Figure 1* when $LiClO_4$ was mixed with PDC_6. Dissociation of the salts seems to be affected by those crown rings with a much larger cavity size than the radius of the cation being considered.

Finally, the ionic conductivity of the PDC_7/P(MEO–MAAM) system was analysed. The effect of the cation radius on the ionic conductivities of P(MEO–MAAM), both in the presence and absence of PDC_7, is summarized in *Figure 5*. However, although reduction of the ionic conductivity of P(MEO–MAACs) was expected in the presence of PDC_7, only a small difference between the Cs^+ ionic conductivities was found (as seen in *Figure 5*). A decrease in the specific interaction might be due to the relatively higher conformational freedom of the crown rings, although details of this are still unclear.

In general it should be noted that the ionic conductivities of the P(MEO–MAAM) materials having the smaller cations was improved, with the smallest cations showing the greatest improvement in conductivity. This tendency was understandable on the basis of the conflicting effects of the crown ether units, i.e. the dissociation of the salts *versus* the trapping of the cations. The smaller cations might experience a weaker trapping force in spite of an acceleration in the salt dissociation.

CONCLUSIONS

Poly(diaza-3*n*-crown-*n*)s having hydroxyethyl side arms (PDC_ns) were mixed with cation conductive polymers (P(MEO–MAAM)s) to show decreases in the cationic conductivity through a specific interaction of the cations and the crown ether rings. Since complex formation between the metal cations and the crown ether units was slow, a simple blend of PDC_n and P(MEO–MAAM) did not show any effects of specific interactions between the two components on the ionic conductivity. Post-copolymerization of PDC_n/MAAM complexes and MEO was required in order to clarify the effects of the crown ether units. The presence of K^+ and Na^+ ions showed the largest differences in the ionic conductivities of the mixed system of P(MEO–MAAM) with PDC_6 and PDC_5, respectively. PDC_7 did not show any suppression of the ionic conductivity for the Cs^+ ion system, due to the flexible conformation of the rings. The presence of crown ether units in the polymers was also suggested as being responsible for accelerating the dissociation of the salts with cations that were smaller than the crown ether cavity. The ion conductive polymers provide a polar environment for the ions, leading to naked migration of the latter, thus reflecting their original characteristics. This unique polar environment has great potential for wider use as a novel solvent system.

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