

# Ionic Conductivity of a Novel Solid Polymer Electrolyte

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**ABSTRACT:** A novel kind of solid polymer electrolyte, the solvation unit of which is O=CNHR, has been studied. The effects of host polymer structure, ion species, salt concentration, and plasticizers on ionic conductivity are discussed in detail. The solvability of host polymers is a very important factor that affects the ionic conductivity of electrolytes and is fully decided by the structure of solvation units and their density in polymer chain. The latter two rest with monomers structure and copolymerization ratio. Effects of alkali metal salts and divalent metal salts on ionic conductivity are different because of their different leading factor of cation radius. Salt concentration dependence of ionic conductivity appears as a double-peak shape when alkali metal salts are added because of the total contribution of two kinds of ionic conductance modes, and appears as similar shapes when divalent metal salts are added. Different influences of plasticizers on ionic conductivity result from their different action ways. Ethylene glycol acts well because of its effective action from three different modes. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2176–2184, 2001

**Key words:** solid polymer electrolytes; ionic conductivity; solvation units; plasticizer; salt concentration dependence

## INTRODUCTION

Solid polymer electrolytes (SPE) are still among the most intensively studied solid ionic conductors because of their potential applications as solid electrolytes in high-energy density rechargeable batteries and other electrochemical devices.<sup>1–3</sup> The main advantages of SPE are their good mechanical properties, ease of fabrication of thin films of desired sizes, and their ability to form proper electrode-electrolyte contact.

Poly(ethylene oxide) (PEO), the solvation unit of which is CH<sub>2</sub>CH<sub>2</sub>O (EO), in particular is an exceptional polymer that dissolves high concentrations of a wide variety of salts to form SPE. Most of the studies in this field are devoted to

PEO-based electrolytes using alkali salts. From the viewpoint of application as well as theoretical considerations, the ionic conductivity is the most important property of SPE. Now the major works still focus on improvement of ionic conductivity of SPE at room temperature on condition that moderate mechanical properties have been gained. And the most commonly studied host polymers such as polyoxa-alkanes, polyesters, and polyethers are mostly based on solvation units EO.<sup>4–6</sup>

In the present article, we report on a novel SPE based on amide that are prepared through the redesign of a new kind of solvation unit O=CNHR, different from the traditional EO unit. The host polymers are obtained by solution copolymerization using acrylamide (AM) as the first monomer, acrylic acid (AA) derivants and butadiene acids as the choice monomers. Alkali salts and divalent metal salts are selected as ionic dopants. Polyatomic alcohol, such as glycerol

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(GROL) and some solvents with strong polarity, are used as plasticizers.

## EXPERIMENTAL

### Materials

AM was obtained from Fluka Chemical Corporation (Switzerland). AA, methyl acrylate (MA), and 2-hydroxyethyl methacrylate (2-HEMA) were distilled before use. Fumaric acid and maleic acid were analytical reagents and used directly without further purification. All ionic dopants and polyethylene glycol (PEG)20000 were refined before use and GROL, etc. liquid plasticizers, were used after distillation.

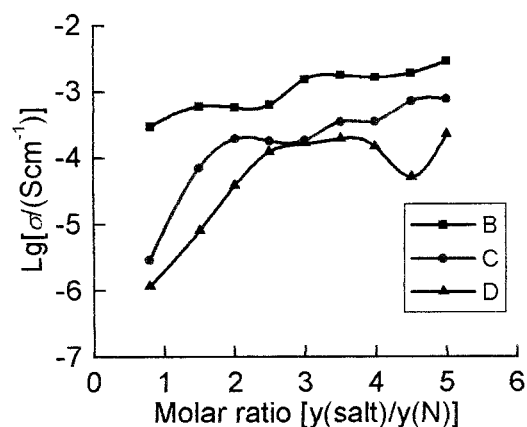
### Polymerization and Preparation of Electrolyte Films

Copolymers were obtained from radical chain copolymerization. Poly(acrylamide-acrylic acid) (PAMAA), poly(acrylamide-methyl acrylate) (PAMMA), and poly(acrylamide-2-hydroxy-ethyl methacrylate) (PAM2-HEMA) were similarly synthesized according to the method reported previously.<sup>7</sup> Ammonium persulfate was used as an initiator and its concentration was controlled 0.04–0.05% of the whole weight of materials when the reaction temperature was controlled at 60°C. All copolymers, PAMAA, PAMMA, and PAM2-HEMA were obtained at the same copolymerization ratio of 6:1 when the effect of comonomers' structure on ionic conductivity of complex systems was considered.

After extensively purified by deposition and carefully dried, the copolymer was mixed thoroughly with metal salt and plasticizer, and stirred 4–8 h under nitrogen atmosphere. The solution was cast on a glass board, then put under the light of an infrared lamp until the films were formed. The films were put into a 60°C constant temperature oven and a 40°C vacuum oven successively to dry for 48–72 h and 24–48 h, respectively. Then a kind of soft and thin SPE membrane was obtained.

### Ionic Conductivity Measurements

The alternating current impedance ( $z$ ) of samples was measured by electrocardiogram electrodes electrical properties measuring apparatus (made by Biomedical Engineering Institute of the Chi-



**Figure 1** Effect of monomer species on ion conductivity of electrolytes. B, PAMAA-MgCl<sub>2</sub>; C, PAMMA-MgCl<sub>2</sub>; and D, PAM2-HEMA-MgCl<sub>2</sub>.

nese Academy of Sciences), and their thickness and area were accurately determined by a micrometer. The ionic conductivity ( $\sigma$ ) was calculated according to the following equation:

$$\sigma = d/(zs) \quad (1)$$

where  $\sigma$  is ionic conductivity (S/cm),  $d$  and  $s$  are thickness (cm) and area (cm<sup>2</sup>) of films, respectively.

## RESULTS AND DISCUSSION

### Structure of Host Polymers

To act as the basis of a polymer electrolyte, a host polymer first must be capable of dissolving salts and must therefore contain solvation units, which can undergo suitable bonding interactions with ions. Second, it must have a structure that has low barriers to bond rotation so that segmental motion of the polymer chain can facilitate the ion transport; specifically, it must have moderate chain flexibility and low glass transition temperature,  $T_g$ . The above two are directly interrelated with the whole structure of host polymers. Polymers copolymerized from different monomers have solvation units with different structure and the corresponding polymer-salt complex systems have widely divergent ionic conductivity. Figure 1 is a curve of the change of ionic conductivity of PAMAA-MgCl<sub>2</sub>, PAMMA-MgCl<sub>2</sub>, and PAM2-HEMA-MgCl<sub>2</sub> with the increase of the value of

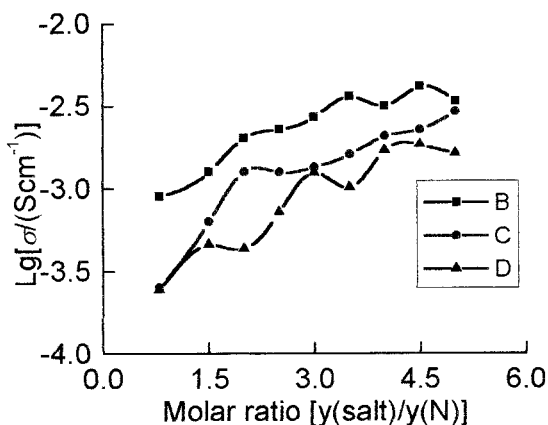
$y(\text{salt})/y(N)$ . Here,  $y(\text{salt})/y(N)$  is the molar ratio of metal salts and solvation units. Ionic conductivity sequence of these three complexes is shown as follows:  $\sigma(\text{PAMAA-MgCl}_2) > \sigma(\text{PAMMA-MgCl}_2) > \sigma(\text{PAM2-HEMA-MgCl}_2)$ .

Ion conductivity of PAMAA-MgCl<sub>2</sub> is obviously higher than that of PAMMA-MgCl<sub>2</sub> and PAM2-HEMA-MgCl<sub>2</sub>, which is directly correlated with the monomer's species. Polymer structure is decided by monomer structure, which is a crucial factor that decides whether the ions can be well dissociated and transfer easily. Chain structure determines rigidity and flexibility of polymers. High flexibility is helpful to segmental movement of polymer chain; that is to say, helpful to decline the resistance to ionic transference. Structure of comonomers determines structure and thus solvability of solvation units. Solvation units in polymer chain are beneficial to dissociation of salts and ions' association and redissociation. The higher solvability is, the better the effect is.

If the chemical formulation of monomers is CH<sub>2</sub>=CR<sub>1</sub>COOR<sub>2</sub>, R<sub>1</sub> and R<sub>2</sub> respectively represent H and H, H and CH<sub>3</sub>, CH<sub>3</sub>, and CH<sub>2</sub>CH<sub>2</sub>OH when the monomers are AA, MA, and 2-HEMA. Different substituent groups R<sub>1</sub> and R<sub>2</sub> result in high or low ionic conductivity of complexes. With the increase of concentration of salt added, the crystalline phase appears first in the complex PAMAA-MgCl<sub>2</sub>; that is to say, the dissolving capability of PAMAA is weaker than that of PAMAA and PAM-2-HEMA, which is due to no side substituents in AA. But it has solvation units with strong polarity, which is helpful to dissociation of salts and transference of ions.

The polycondensation of functional groups is decided by their polarity. It is obvious that the polarity of —OH, —OCH<sub>3</sub>, and —OCH<sub>2</sub>CH<sub>3</sub> groups is degressive in turn, —COOH is an acidic group, and —NH<sub>2</sub> is basic. It will be beneficial to form imide units if CH<sub>2</sub>=CH—COOH is chosen as one monomer. There is little chance to form imide when MA or 2-HEMA is used as the second monomer. The adjacent negative units —COOR and —CONH<sub>2</sub> have some solvability, so that the complexes still have high ionic conductivity (compared with PEO systems) after salts are added.

Copolymerization ratio of monomers will affect sequence distributing of host polymers; specifically, will affect the density of solvation units in copolymers' chain. Figure 2 shows the change of ionic conductivity of three complexes (AM/AA = 2:1, 4:1, 8:1) with the increase of molar ratio



**Figure 2** Effect of copolymerization ratio on ion conductivity of electrolytes. B, AM/AA = 2:1; C, AM/AA = 4:1; and D, AM/AA = 8:1.

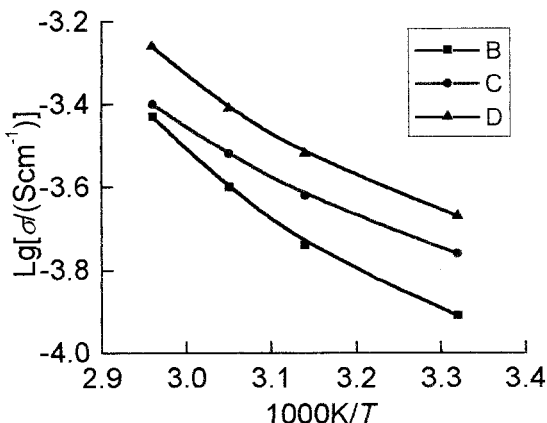
$y(\text{salt})/y(N)$ . PAMAA-MgCl<sub>2</sub> (AM/AA = 2:1) has the highest ionic conductivity and PAMAA-MgCl<sub>2</sub> (AM/AA = 8:1) the lowest. Host polymer copolymerized from a moderate AM/AA value will be liable to have a structure with enough amount of solvation units. Their high ionic conductivity is attributed to their high density of solvation units in polymer chain. When the copolymerization ratio of AM/AA is 2:1, the solvation unit imide is liable to be formed in the polymer chain and its content is high. This improves the solvability of host polymer and thus the ionic conductivity. When the copolymerization ratio of AM/AA is 8:1, the content of AM is comparatively excess, and this goes against the formation of solvation unit, and it is undesirable to gain a high content of solvation unit in polymer chain. So PAMAA (AM/AA = 8:1) has weak solvability and the corresponding complex PAMAA-MgCl<sub>2</sub> (AM/AA = 8:1) has low ionic conductivity.

Furthermore, copolymerization ratio of monomers will also affect the chain flexibility of the host polymer. And the latter will affect ion transference and thus the ionic conductivity. But in a series of copolymers, PAMAA with different copolymerization ratios, the chain flexibility is not as important a factor as the density of solvation unit when their effects on ionic conductivity are concerned.

## Ion Carriers

### Effect of Salt Species

Effects of alkali metal salts on ionic conductivity are different because of their different cation ra-



**Figure 3** Effect of alkali metal salts on ion conductivity under different temperatures. B, LiCl; C, KCl; and D, NaCl.

dius, crystal lattice energy, and ionic mobility. Figure 3 shows the effect of kinds of alkali metal salts on ionic conductivity of electrolytes under different temperatures. The ionic conductivity sequence of the three complexes with added different salts at the same temperature can be shown as follows:  $\sigma(\text{PAMAA-KCl}) > \sigma(\text{PAMAA-NaCl}) > \sigma(\text{PAMAA-LiCl})$

The three salts have different lattice energy, but the difference is small. Specifically, the dissociation degrees of the three salts are of almost no difference under a similar solvent circumstance. The radius of  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  ions is respectively 68 pm, 97 pm, 133 pm, and the radius of anion  $\text{Cl}^-$  is the same. The cation radius seems to become the major factor that affects ionic conductivity of these complexes. The larger  $1/(r_a + r_c)$  value the salt has, the lower is the ionic conductivity of the complex film, where  $r_a$  and  $r_c$  represent the radii of anion and cation, respectively. Ionic conductivity in SPE seems to result from the hopping of carrier ions.<sup>8</sup> The most stable hopping sites are considered to be ion site with the opposite charge of each ion. If one ion pair is formed in the process of ion hopping, the energy necessary for ion separation is shown in the following equation:

$$E = e^2/[4\pi\epsilon_0\epsilon(r_a + r_c)] \quad (2)$$

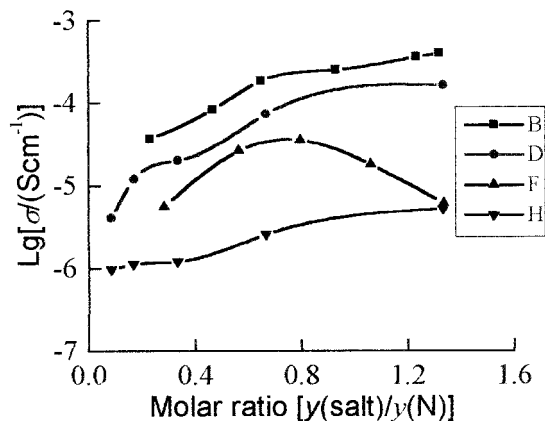
where  $e$  is the charge of the ion,  $\epsilon_0$  is the vacuum dielectric constant, and  $\epsilon$  is the dielectric constant. Consequently, the  $1/(r_a + r_c)$  value of the salt can be a guide for the interaction between

carrier ions in SPE at the same alkali metal salt concentration. As the  $1/(r_a + r_c)$  value decreases, the interaction decreases, resulting in an increase in ionic conductivity.

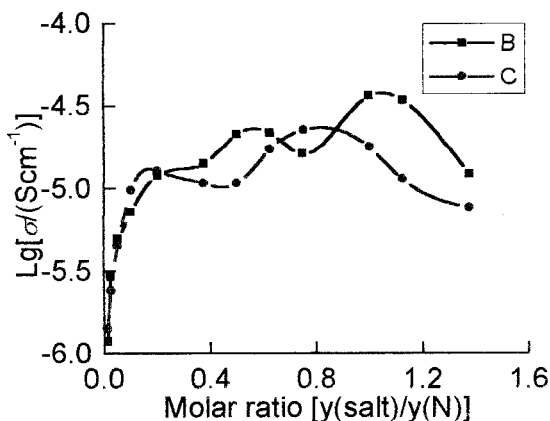
However, KCl has low lattice energy (702.92 kJ/mol) and is liable to dissociate when dissolved in the complex system. At the same time, the ionic mobility of  $\text{K}^+$  (0.762) is almost twice than that of  $\text{Li}^+$  (0.388). By virtue of its high charge density, the  $\text{Li}^+$  ion has the strongest interaction with both host polymer and  $\text{Cl}^-$  counterion, and  $\text{K}^+$  has the weakest interaction. The energy barrier to redissociation should therefore lie in the order  $\text{LiCl} > \text{NaCl} > \text{KCl}$ , whereas the ionic conductivity should lie in the reverse order, as is observed experimentally (shown in Fig. 3).

The effect of divalent metal ionic species on ionic conductivity is shown in Figure 4. The ionic conductivity sequence of four complexes is shown as following:  $\sigma(\text{PAMAA-MgCl}_2) > \sigma(\text{PAMAA-CaCl}_2) > \sigma(\text{PAMAA-SrCl}_2) > \sigma(\text{PAMAA-ZnCl}_2)$ .

Different from alkali metal salts, here cation radius affects ionic conductivity in another way. Generally speaking, when the ions of inorganic salts move through complex systems, an increase in their radius or charge carried will decrease the ionic conductivity. The cation with the smaller radius is easier to be solvated and helpful to diminish resistance of ionic transference and the corresponding complex has higher ionic conductivity. It is well known that small cation means high lattice energy when the anion is the same. But here the former predominates over the latter, resulting in an increase in



**Figure 4** Effect of divalent metal salts on ion conductivity at low molar ratio. B,  $\text{MgCl}_2$ ; D,  $\text{CaCl}_2$ ; F,  $\text{SrCl}_2$ ; and H,  $\text{ZnCl}_2$ .



**Figure 5** Salt concentration dependence of ion conductivity of electrolytes. B, NaCl; and C, KCl.

ionic conductivity, as is shown in Figure 4.  $\text{Zn}^{2+}$  has smaller radius than  $\text{Ca}^{2+}$ , but  $\text{ZnCl}_2$  has lower solubility in the complex system. The amount of salts participating in dissociation is small so that it cannot provide high ionic concentration to get high ionic conductivity. Besides, the increase of added salts enhances the density of carrier ions and acts as transitory crosslinker, which directly leads to the rigidity of polymer chain, namely, weakens its capability of heat movement hence hinders the ions' transference that is accompanying with the segmental movement of polymer chain. This effect is different when the salts added are different. When  $\text{ZnCl}_2$  is added, the electrolyte films become rigid and crisp; that is to say, their  $T_g$  will increase greatly. Undoubtedly this badly affects the ions' transference in the electrolyte films; thus, PAMAA- $\text{ZnCl}_2$  has the lowest ionic conductivity. Figure 4 also shows that with the increase of salt concentration, the ionic conductivity of PAMAA- $\text{MgCl}_2$ , PAMAA- $\text{CaCl}_2$ , and PAMAA- $\text{ZnCl}_2$  increases whereas that of PAMAA- $\text{SrCl}_2$  appears as a peak shape, namely, shows a maximum value. It is because that crystalline phase appears very early in the complex PAMAA- $\text{SrCl}_2$ , as will be discussed in detail in the latter section.

#### Effect of Salt Concentration

Figure 5 shows the relation between the concentration of alkali metal salts (NaCl, KCl) and the ionic conductivity of complexes. The ionic conductivity increases almost linearly with the increase of salt concentrations at first, declines a

little after it reaches a minor maximum value, then continues to increase linearly until it reaches the large maximum value and begins to decline again, that is, forms a double-peak shape.

The total ionic conductivity of electrolytes at any temperature may be given by the equation:

$$\sigma = \sum n_i q_i \mu_i \quad (3)$$

where  $n_i$  is the number of carriers of type,  $i$  in unit volume,  $q_i$  is their electric charge,  $\mu_i$  is their ionic mobility, and the summation is taken over all charged species.

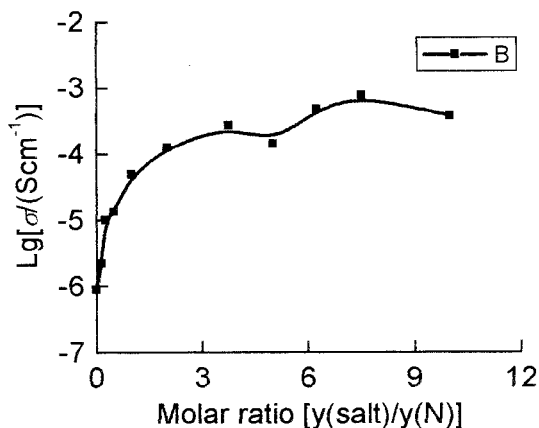
Barker and Thomas<sup>9</sup> have given the following expression:

$$n = n_0 \exp(-W/2\epsilon kt) \quad (4)$$

where  $n_0$ ,  $k$  are constant,  $\epsilon$  the dielectric constant, and  $W$  is the ionic dissociation energy. Salts dissolved in the complex systems dissociate and generate carrier ions. The increase in the salt concentration enhances directly the number of carrier ions, which results in an increase in ionic conductivity. The salts can dissolve fully in the complex systems at low concentration and the ions are easy to transfer because of low ion concentration. In the course of the increase in salt concentration, the number of carrier ions from dissociation increases, and results in the increase of ionic conductivity directly. At the same time, the ionic conductivity of the system will be hindered because of some or all of the following:

1. The presence of the salt added leads to salt-polymer or cation-dipole interaction, which increases the cohesive energy of the system, decreases the free volume fraction, and hinders the segmental movement and thus the ionic mobility.
2. The  $T_g$  of the system becomes higher because of similar reasons, which makes the motion of the polymer chain less mobile.
3. The percentage of associated ion, ion pairs, and triples become higher.
4. Ions act as a transient crosslinking agent.
5. Ions are liable to interact strongly with the acid radicals when both concentrations are high.





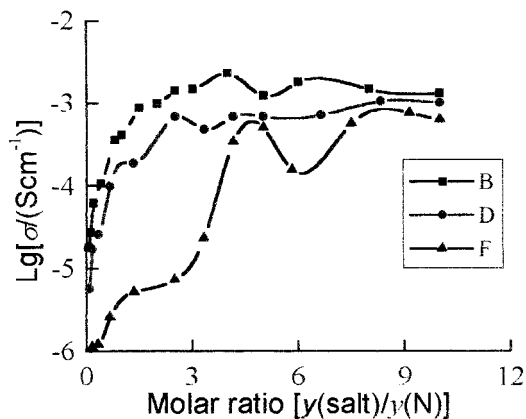
**Figure 6** Salt concentration dependence of ion conductivity of electrolytes. B, LiCl.

The appearance of the minor maximum value of ionic conductivity may be attributed to the above two kinds of opposite effects. The complex is not full amorphous and begins to form crystalline phase with the continued increase of salt concentration. In fact, the films are not so transparent, the salts will separate out in some time, and the viscoelasticity of films declines sharply. In this time, there are two kinds of conductance modes: 1. in amorphous phase, ions conduct through dissociation and coordination to transfer with the segmental movement of polymer chain, and 2. hopping conductance mechanism taking place in the crystalline phase.

The mechanism of the ionic conduction in the amorphous phase follows the free-volume theory, which means that the transport of carrier ions cooperates with the segmental motion of the host polymer. In such a case, it is known that the easier the segmental motion of the host polymer becomes (i.e., the lower the  $T_g$  becomes), the higher the ionic conductivity becomes. The mechanism of the ionic conduction in the crystalline phase is the typical conduction mode in traditional PEO-salt systems. Differential scanning calorimetry analysis proves that with the increase of salt added, the  $T_g$  of the system increases and the system will change from amorphous phase to crystalline phase.<sup>7</sup> For polymer electrolytes, the ionic mobility is closely related to the motion of the host polymer, i.e., the carriers are repeatedly associated with and then dissociated from the ligands formed by moving segmental chains. Crystalline phase means weak segmental mo-

tion and low ionic mobility. It has been suggested that migration of cations is essentially easier in the amorphous phase than in the crystalline phase. Thus, the mixed contribution of two conductance modes leads to the appearance of the large maximum value of ionic conductivity. After the maximum point, the increase of crystalline phase percentage makes the polymer chain rigid, reduces its conductivity in amorphous phase, and results in the decline of ionic conductivity. If too much salts are added, the films will be rigid, opaque, and full of salts separated out, with no adherence so that they cannot adhere tightly to the electrodes, and most of all, have very low ionic conductivity.

Solubility of salts added in complex systems is another important factor that affects ionic conductivity of complexes when the salt concentration increases. Figure 6 shows the effect of salt concentration on ionic conductivity when the salt added is LiCl. The salt concentration dependence of ionic conductivity of complex PAMAA-LiCl also shows a double-peak shape, because of similar reasons. LiCl has high lattice energy and thus low dissociation degree in complex system. But  $\text{Li}^+$  ion is likely to be more strongly solvated than either  $\text{Na}^+$  or  $\text{K}^+$  ions, as indicated by the generally greater solubility of LiCl in the system. The greater solubility means that the total ion number from its dissociation is more. Hence, the ionic conductivity of PAMAA-LiCl reaches  $7.69 \times 10^{-4}$  S/cm at high salt concentration, whereas NaCl and KCl have separated out as a crystalline phase at this salt concentration and have very low ionic conductivity.



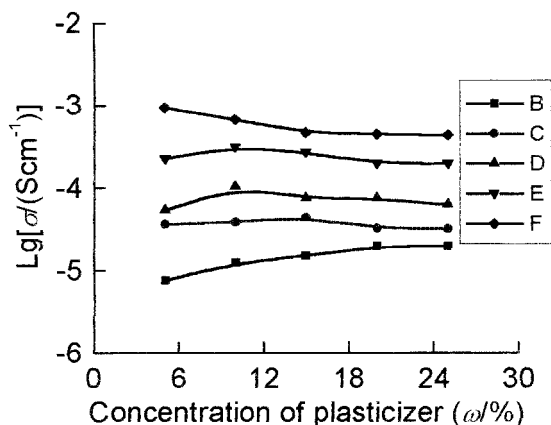
**Figure 7** Salt concentration dependence of ion conductivity of electrolytes. B,  $\text{MgCl}_2$ ; D,  $\text{CaCl}_2$ ; and F,  $\text{ZnCl}_2$ .

Figure 7 shows salt concentration dependence of ionic conductivity of complexes when  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{ZnCl}_2$  are used as ionic dopants. The curves of salt concentration of ionic conductivity of the three complexes also appear as a similar double-peak shape. This should attribute to the mixed conductance modes in these systems. Similar to  $\text{LiCl}$ , despite the high lattice energy and low dissociation degree,  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{ZnCl}_2$  have higher solubility in the complexes than those of  $\text{NaCl}$  and  $\text{KCl}$ , etc. salts with low lattice energy, and their total numbers of ion carriers are more. Hence, the ionic conductivity of  $\text{PAMAA-MgCl}_2$ ,  $\text{PAMAA-CaCl}_2$ , and  $\text{PAMAA-ZnCl}_2$  reach respectively  $2.32 \times 10^{-3}$  S/cm,  $1.06 \times 10^{-3}$  S/cm, and  $7.69 \times 10^{-4}$  S/cm at high salts concentration. The curves of salt concentration of ionic conductivity of  $\text{PAMAA-SrCl}_2$  shows a single peak shape, namely, only a maximum value (shown in Fig. 4). This is because  $\text{SrCl}_2$  has very low solubility in the complex system. During the course of increase of concentration of  $\text{SrCl}_2$ , the crystalline phase appears in the complex film, viscoelasticity is gradually lost, and conductivity is damaged severely. Likewise, the relatively low solubility of  $\text{ZnCl}_2$  in the system is the direct root of the fact that the ionic conductivity of  $\text{PAMAA-ZnCl}_2$  is lower than those of  $\text{PAMAA-MgCl}_2$  and  $\text{PAMAA-CaCl}_2$  in a wide scope of salt concentration. From the above, a conclusion can be drawn that in order to prepare polymer electrolytes with good comprehensive performances, the solubility of salts in complex system should be considered when the salts are added and a kind of host polymer with high solubility capability should be selected

#### Effect of Plasticizer on Ionic Conductivity

The lattice energies of the added salts and the dielectric constant of the host polymers mainly affect the salts' dissociation. To improve the later, two ways are taken: one is the incorporation of negative units with high dielectric constant into the polymer chain; the other is the addition of moderate plasticizers with high dielectric constant into the complex systems.

Dimethyl sulfoxide (DMSO), dimethylformamide (DMF), PEG20000, ethylene glycol (EG), and GROL are used as plasticizers,  $\text{LiCl}$  as added salt, PAMAA as host polymer and different complex systems with different amount and kind of



**Figure 8** Effect of different plasticizers on ionic conductivity of electrolytes. B, PEG; C, DMSO; D, DMF; E, GROL; and F, EG.

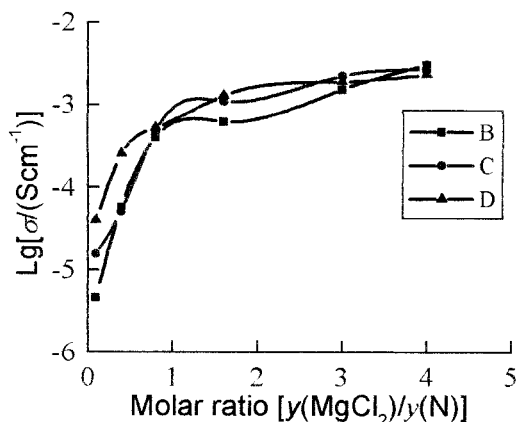
plasticizers are gained. Figure 8 shows the effect of plasticizers on ionic conductivity. It shows that the effect of EG is the best and PEG is the worst.

Plasticizers take an important part in decreasing the dissociation energy of inorganic salts, enhancing ionic conductivity, and improving processability. Generally, plasticizers are helpful to improve the complexes' ionic conductivity in two sides: one is to increase the number of total carrier ions  $n$ , the other is to enhance the flexibility of polymer chain and decline the resistance to ion's transference, that is, to improve ionic mobility  $\mu$ . DMF, DMSO, etc. plasticizers with strong polarity are added to improve the dielectric constant of systems, reinforce interaction with cations, increase salts' dissociation degrees, which leads to the increase of the carrier ion's number. EG, GROL, etc. plasticizers are added to decrease the  $T_g$  of the complex systems, increase the mobility of polymer segments, decrease the resistance to ion's transference, and improve ionic mobility. At the same time, EG and GROL have abilities of "dissolve salts," which may increase salts' solubility in complex systems, that is, increase the concentration of salts that may take part in dissociation, thus increase the carrier ion number. Their most effective effects are attributed to their action through the above two ways. Moreover, these two plasticizers can improve greatly the ionic conductivity of complexes even if the added amount is small, and they are high boiling-point solvents without bleeding during processing. They should be very useful plasticizers in improving ionic conductivity of polymer

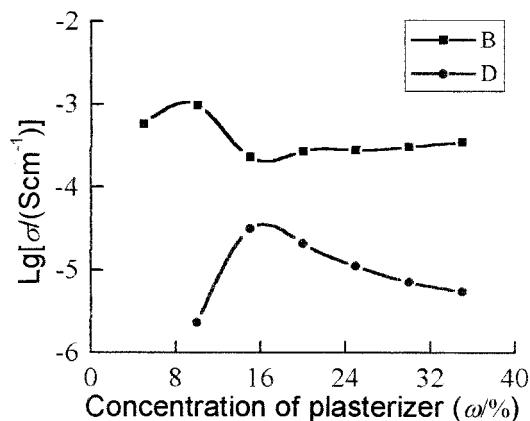
electrolytes. Though theoretically the longer PEG segment is more flexible and gives rise to higher segmental mobility, PEG20000 cannot act well because its chain is too long to affect from the above two sides.

It is also shown in Figure 8 that five kinds of plasticizers affect best when the amount is 10%. The reasons are that if the added amount is too much, the plasticizers will compete with the solvation units in polymer chain, they can enclose the carriers and dilute the concentration of carriers, which restricts the carrier ion transference along with the segmental movement of polymer chain; this results in the decrease of ionic conductivity. The detailed analysis of competition between plasticizers and solvation units can be found in the literature.<sup>10</sup>

Figure 9 shows how three kinds of plasticizers (DMF, DMSO, EG) affect the ionic conductivity of complexes PAMAA-MgCl<sub>2</sub> with different molar ratio  $y(\text{MgCl}_2)/y(N)$ . With the increase of molar ratio  $y(\text{MgCl}_2)/y(N)$ , the ionic conductivity of complexes with different kinds of plasticizers increase also. It is also shown that the effectiveness consequence is EG > DMSO > DMF, though the difference of their effects is not more obvious than that in the PAMAA-LiCl complex system. The explanation is similar to the above. Another reason is that DMF and DMSO are high volatility liquids and easily escape in the course of preparation of complex films. It can be concluded that a special formulation should be designed and selected as to a certain cation. It not only means that comonomers should be well selected to gain a solvation unit with good solvability, but also a



**Figure 9** Effect of plasticizer on conductivity. B, DMF; C, DMSO; and D, EG.



**Figure 10** Effect of the kind of plasticizer on conductivity. B, MgCl<sub>2</sub>; and D, SrCl<sub>2</sub>.

plasticizer to act well on the cation and polymer chain.

Figure 10 shows the change of ionic conductivity of different complexes with the concentration of plasticizer EG. The change rule is different as the salt added is different. At low salt concentration, the plasticization is obvious and the ionic conductivity is effectively improved. At high salt concentration, the ionic conductivity is affected little by the plasticizer or descends. If the amount of plasticizer is excess, it will be easy to be transudatory and cause the inequilibrium in the complex films. This obstructs the ions' transference and causes a bad effect on the chemical and electrochemical stabilities of polymer electrolytes.

## CONCLUSIONS

As a basic matrix of SPE, host polymers should have certain chain flexibility and moderate density of solvation units. Some side groups or proper crosslinking density will provide enough free volume for ion transference and the segment movement of polymer chain. Efficiency of plasticizers and the consistence between plasticizers and host polymers must be considered when plasticizers are chosen because their major action is to be helpful to the dissociation of metal salts and transference of ions. As for the salts, they should have low lattice energy and good solubility in complex systems to get enough ion numbers for high ionic conductivity.

The favorable ionic conductivity of this new kind of SPE is attributed to the redesign of novel



solvation unit O=CNHR with good solvability and the selection of a reasonable component formulation. The electrolyte film has been used in the fabrication of disposable electrocardiogram electrodes that will have great use in clinical diagnosis.<sup>11</sup> The electrodes have advantages such as clear low alternating current impedance, excellent time stability, and improved stimulated defibrillation recovery.

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