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Electrical conductivity of poly(ethylene oxide)–alkali metal salt systems and effects of mixed salts and mixed molecular weights

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The structure and conductivity of mixtures of poly(ethylene oxide) (PEO) with a molecular weight (*MW*) of 4 000 000 and KSCN vary with salt concentrations. The PEO–KSCN material of a molar ratio ethylene oxide unit to cation (O/K^+) of 16/1 has low conductivity, and its crystal structure is similar to that of pure PEO, but with a lower crystallinity and melting point. The 8/1 material shows a high conductivity and exhibits an almost completely amorphous state, but the 4/1 material has a very low conductivity and a completely different crystal structure with a very high melting temperature. Mixed salt (LiSCN–$NaClO_4$) systems increase the conductivity. It is suggested that these results can be explained in terms of molecular disorder in the PEO–salt phase, configurational entropy and/or degree of salt dissociation. Mixed anions (KSCN–KI) can also increase conductivity in systems having a high proportion of the SCN^- ion. PEOs with a *MW* of 600 and 18 500 show a possible application as plasticizers to increase conductivity, due, in part, to the higher content of hydroxyl end-groups to dissociate the salt into free ions and, in part, to the lower glass transition temperature (T_g). PEO (*MW* 600) gives a better result than PEO (*MW* 18 500) at the same proportion in the two *MW* systems. A blend of three molecular weights (4 000 000, 18 500 and 600) has a higher conductivity and a lower crystallinity than do blends of two molecular weights. These phenomena are discussed in terms of random coil behaviour or the lack of it for the lower molecular weight species. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(ethylene oxide); blends; electrical conductivity; ionic conduction; polymer–salt alloys)

INTRODUCTION

Polyether-based electrolytes have been studied since the work of Wright[1,2]. The potential use of these materials in battery applications was first studied by Armand *et al.*[3]. The most important factor in the polymer–salt complex formation is the energy requirement. A negative change of free energy is required. In addition to the energy requirement, the possibility of complex formation can be predicted by the hard–soft acid–base principle suggested by Pearson[4]. The hard acids and bases are small, of high electronegativity (electrons held tightly), of low polarizability and hard to oxidize, but the soft ones are the opposite. Hard acids prefer to react with hard bases, and soft acids with soft bases. So the hard base ether oxygen in PEO can form a stable complex with hard acids. The strong attractive force in the stable complex will make the cations immobile[5].

In the two regions of semicrystalline polymers, crystalline and amorphous regions, ions prefer to dissolve in the amorphous phase[6,7]. At low salt concentrations, no crystalline complex can be observed; this means that the salts are dissolved in the amorphous phase. At salt concentrations higher than the solubility limit of semicrystalline PEO, a crystalline complex is formed. Ions can move in the amorphous phase easily because of the low energy barriers.

When salt dissolves in polymer and dissociates to ions, it generates carrier ions and increases the viscosity simultaneously. These two results have opposite effects on conductivity; the former increases conductivity, while the latter decreases conductivity because the ions act as a transient cross-linking agent that increases T_g, and thereby decrease the ionic mobility.

The effect of anions on conductivity is important, because electrical conductivity is the result of cation and anion flows in opposite directions. In application in batteries, cations from the metal electrode can compensate the polarization of cations, but there is no anion source that can act similarly. If mobile anions are used, the polarization of anions will take place in the system. This polarization causes an anion concentration gradient that affects the conductivity of the system after the battery is used. For this reason, it is better to use medium or large anions of relatively low mobility, such as SCN^-, ClO_4^-, I^-, etc. Furthermore, the salts of small anions have high lattice energies, making the formation of the complex unfavourable.

Kelly *et al.*[8] proposed a structural model for PEO–$LiCF_3SO_3$ = 8/1. Three phases exist in the system: (1) crystalline PEO (lamellar, spherulitic), which is non-conducting, (2) a crystalline complex of PEO and salt (spherulitic), which is poorly conducting, and (3) an amorphous phase (interlamellar, interspherulitic), which is conducting. Increasing the conductivity of polymer electrolytes is related to changing the proportion of each

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phase[9]. At high temperatures the proportion of the amorphous phase is high, corresponding to high conductivity.

Many techniques have been used for the objective of increasing the conductivity of the PEO-based system[10–12]. Blending polymers with other polymers or the same kind of polymer with different molecular weight and adding a plasticizer have been studied. In addition to blending, using a low molecular weight plasticizer to reduce T_g and increase the mobility of polymer chains is a practical way to increase conductivity. However, there are some limitations on using a plasticizer; the non-volatile plasticizer must be completely miscible with the main polymer (to prevent phase segregation) and should not be reactive to electrodes for long-term stability.

Propylene carbonate and low molecular weight poly(ethylene glycol) (PEG) have been studied as plasticizers. Propylene carbonate has the drawback of a high vapour pressure. PEG (*MW* 400) is reactive to lithium, and so a high-resistance interface between the lithium electrode and the electrolyte is formed. The reaction between lithium and the hydroxyl groups at the ends of PEG chains is the cause of this problem. This can be avoided by using dimethyl PEG instead of PEG[8,13] or by using a low percentage of PEG. Low-*MW* PEG gives a higher conductivity due to (1) a lower viscosity and (2) a higher concentration of hydroxyl groups, both features acting to enhance the mobility of the ions, to reduce crystallinity, T_g and the activation energy for ion conduction, and to increase the proportion of the amorphous region and the conductivity.

As the salt concentration is increased, the conductivity of the system increases at low concentrations and then decreases at high concentrations because of the formation of a complex between PEO and the salt. The complex forms when the solubility of the system has been exceeded. From this concept, if two kinds of salt without a common ion are used, conductivity might be increased.

The mixed alkali effect (MAE) refers to the deviation from additivity of a property as a function of the ratio of concentrations of one alkali ion to another, while the total concentration of cations is constant. This has been studied in ionic glass systems. The $0.3[x\text{KSCN}-(1-x)\text{NaSCN}]-0.7\text{Ca(NO}_3)_2\cdot 4.06\text{H}_2\text{O}$ melts showed this effect on fluidity and conductivity[14]. Ingram *et al.*[15] studied the $x\text{K}_2\text{SiO}_3-(1-x)\text{Na}_2\text{SiO}_3-7\text{H}_2\text{O}$ system and found a minimum in conductivity in isofluidity–conductivity plots at low temperatures in the low-fluidity (or high-viscosity) region, because the structural relaxation time $\langle\tau_s\rangle$ is much greater (~100 times) than the conductivity relaxation time $\langle\tau_\sigma\rangle$. No MAE was observed in the high-fluidity (or low-viscosity) region, because the ratio of $\langle\tau_s\rangle$ to $\langle\tau_\sigma\rangle$ was small. The PEO–Na/KSCN and poly(propylene oxide) (PPO)–Na/KSCN systems were studied for the MAE on conductivity[16]. In the PEO system, the conductivity of the mixed-cation system increased when the proportion of K^+ ions increased and showed the MAE in the region of 20–60 mol% potassium, while the PPO–Na/KSCN system showed no MAE. The presence and absence of the MAE in these systems can also be explained in terms of the relaxation times of the local polymer structure and those of ion conduction.

A mixed-anion effect has been studied by Chandra and Chandra[17]. PEO–Na–I/SCN and PEO–Na–I/ClO$_4$ systems showed a non-linear variation between conductivity and the ratio of anions, with a minimum conductivity at 50% mixed anion. The minimum in the I/SCN system was lower than I/ClO$_4$, because the dipole-induced dipole interaction in I^-–SCN^- was higher than that in I^-–ClO_4^-. Thus, some anions may be immobilized by this interaction. The authors also suggested that the mobility of anions in the crystalline phase may be higher than that in the amorphous phase. However, the relationship was not very evident.

Mixed-salt systems showed a higher percentage of the amorphous phase and a higher conductivity than either of the single-salt systems[18,19].

EXPERIMENTAL

Materials

PEO, with a nominal *MW* of 4 000 000 was obtained from Scientific Polymer Products; PEOs with *MW*s of 18 500 and 600 were supplied by Polysciences. Polymers were used as received. KSCN and KI were obtained from Sigma (ACS reagent grade, 100% assay) Anhydrous NaClO$_4$ was obtained from Alfa (ACS reagent grade, 100% assay). LiSCN was obtained from Fluka (practical grade, assay >95% after dehydration). Methanol and acetonitrile were obtained from Aldrich (ACS reagent grade) and EM Science (HPLC grade, 99.8%), respectively.

Sample preparation

Polymer films were prepared by the standard solution technique. The solvent was methanol (unless otherwise noted). Inorganic salts were heated overnight in a vacuum oven to dehydrate the salts. The mixture was stirred at room temperature for 24 h to obtain a homogeneous solution and complete complexing between PEO and the salt. Films were cast on a microscope slide. The polymer mixture was left overnight in a fume hood to let the solvent evaporate. In the case of the KI system, the films were cast in a vacuum oven at low pressure to minimize the oxidation between KI and oxygen in the atmosphere. For LiSCN systems, acetonitrile was used, since PEO cannot dissolve in a LiSCN–methanol mixture and it cannot generate a homogeneous solution even at high temperature (such as 50°C).

Conductivity measurement

The impedance of the film was measured using a Hewlett Packard 4274A multifrequency LCR meter (with a frequency range of 100 Hz to 100 kHz). The voltage across the stainless steel electrodes was fixed at 0.2 V throughout the experiments, because there is neither oxidation nor reduction of ions in the electrolytes at this low voltage. Bulk resistance is defined as the real axis intercept of the impedance plot.

Differential scanning calorimetry

A Du Pont Instruments 9900 Thermal Analysis System was utilized to measure T_g and T_m. All samples were heated in a vacuum oven overnight at 120°C to ensure dehydration of the specimens. D.s.c. scans were performed in an N_2 atmosphere. The heating rate was $10^\circ\text{C min}^{-1}$. To perform the d.s.c. scan to find T_g, the system was first cooled to a very low temperature by

Table 1 Conductivities of the materials at various salt concentrations

Specimen PEO–KSCN	Conductivity ($S cm^{-1}$)
16/1	1.5 ($\pm$0.2)$\times 10^{-6}$
8/1	3.1 ($\pm$0.3)$\times 10^{-6}$
4/1	8.0 ($\pm$0.3)$\times 10^{-7}$

Table 2 Melting temperatures and percentage crystallinity of specimens

Specimen	T_m (°C)	ΔH ($J g^{-1}$)	crystallinity (%)
PEO 4 000 000	67	155	83.0
PEO 18 500	60.5	168.3	89.5
PEO–KSCN 16/1	54.7	48.4	25.7
PEO–KSCN 8/1	–	–	–
PEO–KSCN 4/1	106.3	56.36	–

liquid nitrogen. The crystallinity of PEO can be calculated by comparing the measured heat of melting to that of 100% crystalline PEO. The reported value of ΔH_m of 100% crystalline PEO is $45 cal g^{-1}$ or $188.1 J g^{-1}$ [20].

X-ray diffractometry

A Philips 3000 X-ray generator was used to give CuKα radiation. Specimens were fixed into an aluminium holder and in a sandwich of Scotch Tape to prevent ingress of moisture. The diffraction patterns of Scotch Tape and the aluminium holder were obtained to act as a baseline reference for the patterns of the specimens. In cases where the specimens were almost amorphous, the tape was not used, and moisture absorbents (silica gel and $CoCl_2/CaSO_4$) were put in the specimen chamber at least 5 h before performing the X-ray diffraction (XRD) to ensure dehydration of the air in the chamber. Diffraction patterns of the blank sample holder with the absorbents inside the specimen chamber were recorded as a baseline.

RESULTS AND DISCUSSION

Effects of salt concentration

The conductivities of the systems are as in *Table 1*.

A trend was observed in which conductivity increased with increasing salt concentration to a maximum, then decreased at very high salt concentrations. The decrease in conductivity in polymer electrolytes has been suggested to derive from one or more of the following: (1) higher T_g of the system[21], which makes the motion of polymer chain less mobile; (2) higher percentage of associated ions, ion pairs and triple ions[22]; or (3) ions acting as a transient cross-linking agent[23].

The appearance of each specimen was as follows:

(a) Pure PEO showed well-defined spherulites and the cast film was opaque and rigid.

(b) The 16/1 film was translucent and rather rigid compared with that of the 8/1 film. Spherulites having shapes similar to those in pure PEO were observed under the microscope. After heating the film at 100°C for 2 h, the film became transparent and flexible; but after keeping at room temperature, the film returned to its original semi-transparent state. The change is reversible.

(c) The 8/1 film was soft, transparent and colourless. After heat treatment, but before conductivity measurement, the film was transparent and colourless but it was less soft, because moisture and residual solvent were evaporated. The surface of the film was smooth. Under a cross-polarized microscope, no spherulites were observed at this composition. The film remained transparent and colourless for more than one month at room temperature. It can be interpreted that the concentration was not low enough to give well-defined spherulites of pure PEO, not high enough to give a crystalline complex of PEO and KSCN, and not too high to exceed the solubility of the salt in the amorphous polymer. An amorphous phase without free salt is desirable for use as a polymer electrolyte. The 8/1 molar ratio equals 11.1 mol% of salt, a concentration that falls within the crystallinity gap area, as shown in the PEO–KSCN phase diagram.

(d) Very fresh 4/1 sample thick film (< 16 h old) was transparent, and a few spherulites were observed under an optical microscope. Within 24 h after casting the film, there were some opaque spots and they extended throughout the film. Salt crystals were at the centres of the spherulites, indicating heterogeneous nucleation. After 2 days, the film was rigid and opaque, and one cannot observe any spherulites and other features with the optical microscope. In some areas of fresh films, salt precipitates in the form of dendrites can be seen. This concentration obviously exceeds the solubility of the salt in the polymer. The film was very rigid and less moisture sensitive.

D.s.c. thermograms of PEO (*MW* 4 000 000)–KSCN specimens at ratios of 16/1, 8/1 and 4/1 were obtained. Information on melting temperatures and crystallinity can be calculated by integrating the area under the melting peak to obtain the endothermic energy change and comparing to a reference value. The percentage crystallinity of each specimen is shown in *Table 2*.

A low-*MW* PEO (18 500) has a higher crystallinity but a lower melting temperature than does a high-*MW* one (4 000 000). The specimen at low salt concentration (16/1) has a lower melting point with a lower crystallinity. It was assumed that the heat of fusion of the PEO–KSCN crystalline phase at the ratio 16/1 equals that of pure PEO. However, the melting point of the 4/1 material is too high to be considered to be the melting of crystalline pure PEO, so it is not possible to calculate the crystallinity at this composition.

The melting temperature of pure PEO (*MW* 4 000 000) is 67°C, while that of a 16/1 mixture is only 55°C. Yang *et al.* have suggested that the cations attract the oxygen atoms and weaken the covalent bonds between carbon and oxygen atoms in the polymer backbone. This effect can explain the lower thermal stability of the PEO–$ZnBr_2$ system[24]. There were no other phase transitions at high temperatures, so no free salts nor crystalline complex existed in the film. The dissolved salts contained within the spherulites melted simultaneously with the polymer. The mixture is stable to at least 250°C, implying a potential application at high temperatures.

There is no strong peak in the d.s.c. trace of the 8/1 system. It can be concluded that the mixture at this composition is completely amorphous. This result is consistent with the crystallinity gap in the phase diagram[25].

For a 4/1 mixture, the salts not only dissolve in PEO, but also form a crystalline complex having a high melting

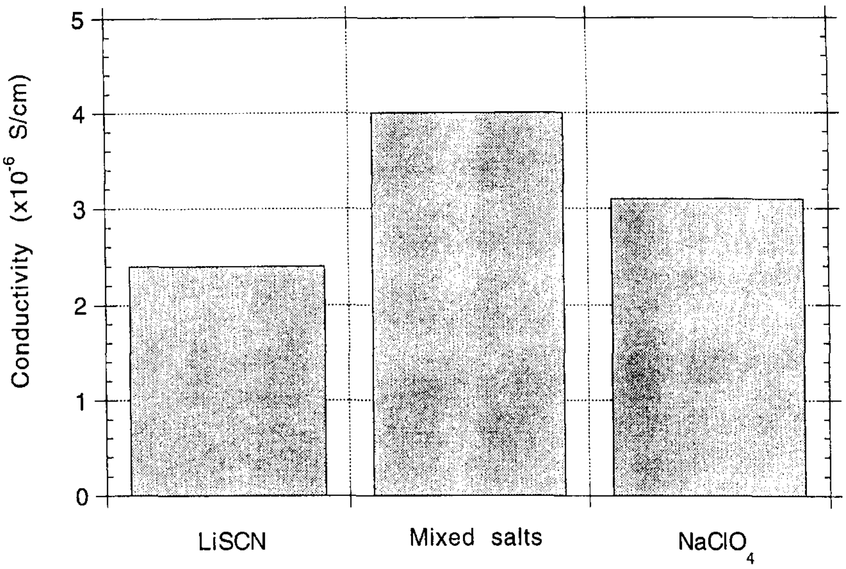

Figure 1 Conductivity of a mixed-salt system, compared to one-salt systems

point (106°C). This effect of mixing at this high concentration is opposite to the case of low salt concentration, which gives a lower melting point phase. The free salts that were observed under the microscope showed a melting peak at 172°C, the melting temperature of pure salt. It is obvious that the solubility limit is exceeded.

In XRD patterns, pure PEO gave two strong peaks, at 19 and 23°, and a doublet at 26.5°. The 16/1 mixture also gave peaks at the same positions, but with lower intensities. This result is further evidence that the melting peak at 60.5°C in d.s.c. came from crystalline PEO, because the pure PEO phase still existed. It can be concluded that the crystalline phase in the film has the same structure as PEO, but at a lower percentage of the crystalline phase. Some portion of the PEO–salt mixture existed as an amorphous phase, and thus did not give a peak in the XRD pattern.

The diffraction patterns of the 8/1 mixture showed a completely amorphous phase. No peaks were observed in the XRD pattern, only a very broad humped baseline, which ranged from 17 to 32°. No peaks of pure KSCN were observed, suggesting no free salt phase. This is the optimal structure for PEO–KSCN as an electrolyte.

The 4/1 mixture showed absolutely different patterns from pure PEO. The peaks at 19 and 23° disappeared, suggesting that there was no free PEO crystalline phase. Many new sharp peaks exist, implying that a new crystalline complex with well-defined structure is present. No peaks of KSCN were observed. Apparently, the number of crystals is not high enough to produce diffraction peaks, although some free salt crystals were observed in the film.

Effect of mixed salts

It was planned that the effects of mixed salts be studied in both KSCN–$NaClO_4$ and LiSCN–$NaClO_4$ systems, but the former failed because there were fine precipitates after mixing both salts in methanol. Separating two salts into two mixtures, PEO–KSCN in methanol and PEO–$NaClO_4$ in methanol, then mixing two mixtures and casting a film of mixed salts can solve this problem to some extent, but the dried film still showed salt precipitates. Acetonitrile was used as a solvent, but this solvent also failed to solve the problem. Thus, preparing the PEO-mixed KSCN–$NaClO_4$ system was unsuccessful for studying the effects of mixed salts at this concentration.

PEO cannot dissolve in an LiSCN–methanol mixture; so acetronitrile was used as a solvent in the LiSCN system. Conductivity of PEO–LiSCN (8/1), PEO–$NaClO_4$ (8/1) and PEO–LiSCN–$NaClO_4$ (16/1/2) films were measured. The results are shown in *Figure 1*. The standard deviation is approximately 0.3×10^{-6} S cm^{-1}. The mixed salts increase the conductivity. The surface features of the film were inspected with an optical microscope, but there was no difference from those of the one-salt systems.

The higher conductivity of mixed-salt systems can be explained in terms of the disorder in the PEO–salt phase, induced by mixing two kinds of salts into the PEO system. There are three possible explanations for this mixed salt effect:

(1) PEO–$LiCF_3SO_3$–NaI systems with EO–salt = 4/1 and 8/1 were studied by MacCallum *et al.*[18,19]. They found that mixed salt systems increased conductivity. ^{1}H n.m.r. was employed to find the percentage of the elastomeric phase and the content of mobile ions in the amorphous phase that can be reflected by the relaxation time T_2 of protons in amorphous chains. T_2 in the mixed-salt material is lower than that in one-salt material, suggesting a higher content of mobile ions in the mixed-salt system. It was also found that the distinction between spherulites and the amorphous phase became blurred. These results suggested that the conductivity improvement was an effect of inducing topological disorder in the polymer through the mixing of salts with different ion sizes and types. This mixing modulated the arrangement of polymer chains and ions, such that the possibility that chains will fold to crystallize was reduced. The consequent increase in the percentage of amorphous phase increased the conductivity.

(2) In addition to the description in terms of molecular disorder, thermodynamics can be applied to describe

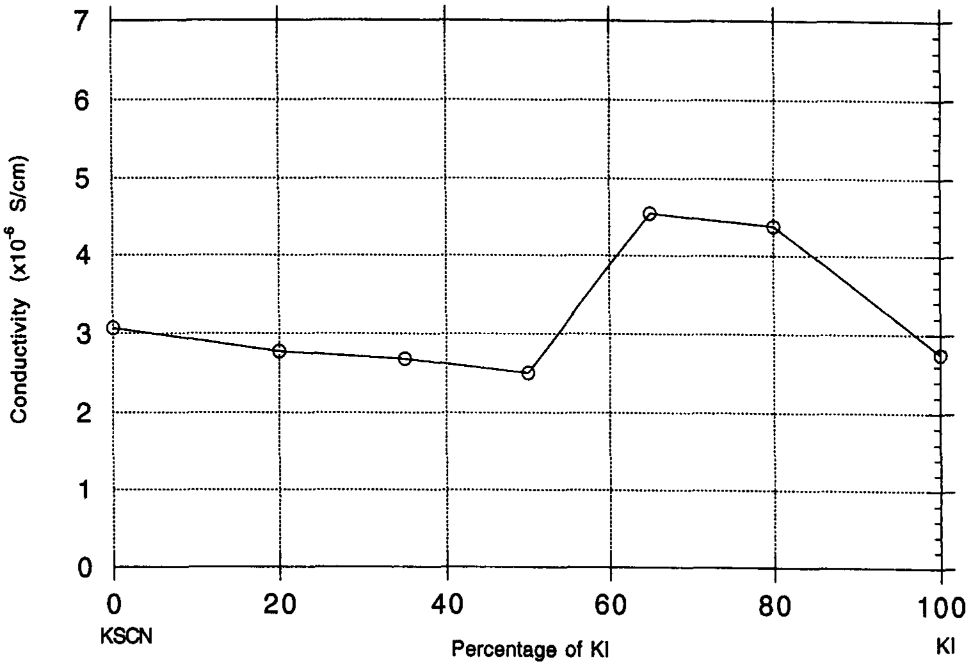

Figure 2 Variation of conductivity with various SCN/I ratios for the PEO–K$^+$ system at a ratio of PEO–K = 8/1

the result. The probability of a mass-transporting cooperative rearrangement, W, was evaluated by Adam and Gibbs[26]:

$$W(T) = A\exp\left[-\frac{\Delta\mu\, s_c^*}{kTS_c}\right] \qquad (1)$$

where A is a frequency factor, $\Delta\mu$ is the energy barrier which hinders the cooperative rearrangements, s_c^* is the minimum configurational entropy required for rearrangement, and S_c is the molar configurational entropy at temperature T.

In terms of statistical thermodynamics, configurational entropy is the degree of randomness:

$$S = k\ln\Omega \qquad (2)$$

where Ω is the number of arrangements in the system. The randomness (configurational entropy, S_c) in the crystalline complex of PEO–salt is low, so the probability of cooperative polymer rearrangement is low. It is expected that cation motion should be coupled with short-range fluctuations of polymer chains, and, consequently, the conductivity should be low[27]. By the same steps of reasoning, it can be argued that the configurational entropy of a mixed-salt system is higher than that of a one-salt system, such that the cooperative rearrangement occurs more easily at the same temperature. The conductivity increment might be explained by this approach.

(3) Another possible reason is associated with the higher degree of salt dissociation into free ions. At the same total salt concentration, using one salt will provide a lower number of free ions than using two salts. High percentages of ion pairing and formation of triple ions exist in systems of pure $LiCF_3SO_3$ and pure $LiClO_4$[18]. The percentage of free ions decreases as the salt concentrations increase. Thus, using two salts at a composition of 16/1 for each salt can increase the percentage of free ions, compared to one salt at a composition of 8/1.

Effects of mixed anions

The effects of mixed anions in PEO–KSCN–KI systems were characterized at various ratios of KSCN to KI. After heating the films having KI at 120°C, the films changed from colourless to yellow. The heating temperature was reduced to 80°C, and the heating time was increased to 30 h to ensure the dehydration of the films. However, the films were bright yellow after heating. The conductivities of the mixtures are shown in *Figure 2*. There are increases in conductivity when KSCN is added to KI, in concentrations of up to 65% KI. Beyond that level, the conductivity drops sharply, followed by a slow increase in conductivity with SCN addition.

This result is identical to what was observed by Chandra *et al.*[17] in the system of PEO–NaSCN–NaI. Since SCN$^-$ is polar (due to the heteroatoms in the anion), the dipole-induced dipole interaction between I$^-$ and SCN$^-$ might immobilize some anions. A decrease in conductivity is distinct at the 50% KI level because of the equivalent number of both anions, and could well be due to such anion association. The non-linear variation of conductivity in the case of the K$^+$ ion here is similar to that observed for the Na$^+$ ion; for Na$^+$ systems there is a linear variation in the region of high percentages of high-conductivity salt (50–100% NaI in NaI–NaSCN and NaI–$NaClO_4$, systems in which NaI has the higher conductivity) and a non-linear variation showing a maximum in the region of low percentages of the high-conductivity salt (0–50% NaI). In this work, the conductivity of KSCN is higher than that of KI, and again a linear variation took place on the side of a high KSCN proportion.

Oxidation of KI in the film might take place to some extent, as indicated by the slightly yellow colour of the film. Films with a high percentage of KI were more yellow. Although the films were transparent after casting in the oven with low pressure at room temperature, the heating of the films might accelerate the oxidation.

Table 3 Conductivity of mixed-*MW* PEO–KSCN systems

System	Conductivity ($\times 10^{-6}$ S cm^{-1})
10 + 0 + 0	3.1 (±0.3)
9 + 1 + 0	3.5 (±0.2)
9 + 0 + 1	4.8 (±0.3)
9 + 0.5 + 0.5	7.3 (±0.4)
8 + 2 + 0	8.2 (±1.2)
8 + 0 + 2	12.6 (±0.9)
8 + 1 + 1	14.3 (±0.9)

Table 4 Glass transition temperatures of pure PEO and mixtures of different *MW* PEO–KSCN specimens

System	T_g range (°C)	$T_{g,\ \mathrm{midpoint}}$ (°C)
pure PEO	−68 to −50	−60
PEO–KSCN 8/1, 10 + 0 + 0	−39 to −33	−35.7
PEO–KSCN 8/1, 8 + 2 + 0	−40 to −35.6	−38.0
PEO–KSCN 8/1, 8 + 0 + 2	−42.1 to −37.9	−40.3
PEO–KSCN 8/1, 8 + 1 + 1	−42.5 to −38.3	−40.2

Table 5 Comparison between ratios of mixed-*MW* PEOs, based on repeat unit and polymer chain

System	Molar ratio based on repeat unit	Molar ratio based on polymer chain
8 + 2 + 0	8/2/0	1/54/0
8 + 0 + 2	8/0/2	1/0/1667
8 + 1 + 1	8/1/1	1/27/833

The cause of this variation, shown in *Figure 2*, is unknown. However, it was proposed that it might be due to variations of crystallinity and ionic mobility.

Effects of mixed molecular weight polymer

Mixtures of KSCN and PEO with mixed molecular weights were studied. Molecular weights of 600, 18 500 and 4 000 000 g mol^{-1} were used. The nomenclature used in referring to these blends is $a + b + c$, where a, b, and c are the weight ratios of molecular weights 4 000 000, 18 500 and 600 g mol^{-1}. The mixture compositions were calculated based on weight fraction (or weight per cent), which is close to the mole fraction of the repeat unit (ethylene oxide). The compositions of the specimens studied were 9 + 1 + 0, 9 + 0 + 1 and 9 + 0.5 + 0.5, and 8 + 2 + 0, 8 + 0 + 2 and 8 + 1 + 1.

Using the PEO with a *MW* of 600 softened the film more than using PEO with a *MW* of 18 500, but there was no difference in other features when using an optical microscope. The conductivities of the mixtures are shown in *Table 3*. It is observed that conductivities of mixed-*MW* PEO–KSCN systems are higher than that which is found if only one *MW* is used. In binary *MW* systems, the PEO with a *MW* of 600 can increase the conductivity more effectively than does a *MW* of 18 500. Increasing the content of low-*MW* PEO in the material enhances the conductivity of the system. It was also observed that using three *MW*s is the most appropriate way to increase conductivity at room temperature.

XRD patterns of specimens 10 + 0 + 0, 9 + 0.5 + 0.5, 8 + 0 + 2 and 8 + 1 + 1 were obtained to examine the effect of low-*MW* PEO on structures. The scattering from the polymer/salt materials is broad and liquid-like. A slight difference in diffraction pattern in the 2θ range of 15–30° between 10 + 0 + 0 and 9 + 0.5 + 0.5 samples could be observed, but this difference was slight. The difference in that range became more evident in the cases of the 8 + 0 + 2 and 8 + 1 + 1 systems. The intensity hump of 8 + 1 + 1 was more featureless than that of 8 + 0 + 2, suggesting that the 8 + 1 + 1 system is more amorphous.

The d.s.c. traces of pure PEO and 10 + 0 + 0, 8 + 2 + 0, 8 + 0 + 2 and 8 + 1 + 1 mixtures were obtained, and the glass transition temperatures are listed in *Table 4*.

Low-*MW* PEO can be used as a plasticizer in PEO-based electrolytes. The liquid PEO softens the film, and the low viscosity of PEO should decrease the energy barrier to ion transport. The conductivity is increased for this reason. Furthermore, the PEG has a much higher content of hydroxyl groups per weight than PEO with high *MW*. The hydroxyl groups dissolve the salts to obtain dissociated ions[28], and this effect also contributes to the increased conductivity shown in *Table 4*. From *Table 4*, it is obvious that dissolved salts increased the glass transition temperatures of the systems. However, T_g can also be decreased by mixing with low-*MW* PEO. The 8 + 0 + 2 system has a lower T_g than the 8 + 2 + 0 system because of the lower *MW* of PEO (*MW* 600) in the former. The 8 + 1 + 1 mixture has a T_g very close to that of 8 + 0 + 2, suggesting the effectiveness of mixing three different *MW* PEOs, as shown previously in the XRD patterns. In other words, for a system having 80% PEO (*MW* 4 000 000) and 10% PEO (*MW* 600), mixing 10% PEO (18 500) gave a better conductivity than adding another 10% more PEO (*MW* 600).

The 8/1 PEO (*MW* 18 500)–KSCN material is liquid at ambient temperature, suggesting that PEO (*MW* 18 500) has potential to be used as a plasticizer. The hybrid films of 9 + 1 + 0 and 8 + 2 + 0 were softened as expected, and conductivity was also increased. The lower conductivities of the 9 + 1 + 0 and 8 + 2 + 0 systems, relative to those of the 9 + 0 + 1 and 8 + 0 + 2 systems, respectively, suggests that PEG (*MW* 600) has an advantage over PEO (*MW* 18 500), because of the higher hydroxyl group content. Increasing the content of low-*MW* PEO resulted in an increment of conductivity, due to the greater plasticizing and dissolution effects. The molar ratios of hydroxyl groups in each mixture are shown in *Table 5*.

From *Table 3*, graphs between conductivity and percentage of low-*MW* PEO are plotted, as shown in *Figure 3*. It is seen in the figure that the relation between conductivity and percentage of added low-*MW* PEO is non-linear.

A relation between conductivity and free volume has been expressed as[29]

$$\sigma = \sigma_0 \exp\left(-\frac{\gamma V*}{V_f} - \frac{\Delta E}{RT}\right) \tag{3}$$

where γ is a numerical factor to correct the overlap of the free volume, V^* is a critical free volume that allows ions to move into the holes of free volume, and V_f is an average free volume per molecule and is temperature-dependent:

$$V_f = V[f_g + \Delta\alpha(T - T_g)] \tag{4}$$

where V is the specific volume at any temperature, f_g is the free volume fraction at T_g, and $\Delta\alpha$ is the

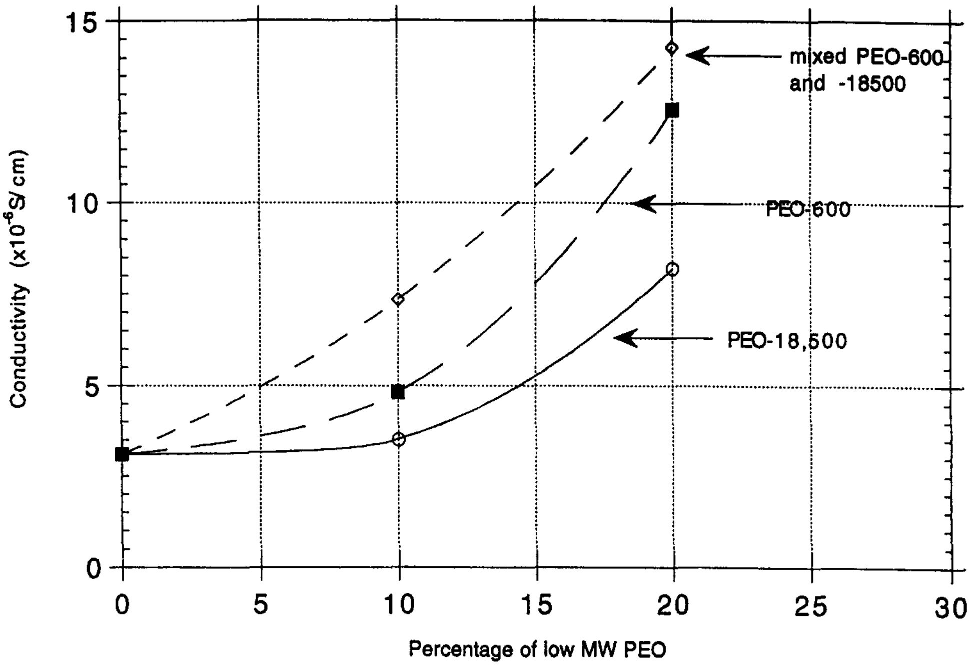

Figure 3 Conductivities of materials having low-*MW* PEOs as plasticizers

difference between the thermal expansion coefficients at temperatures above and below T_g.

It is seen that systems having high V_f have high conductivity. For very low-*MW* PEG (i.e. *MW* 600), the molecules are not long enough to be coiled and entangled polymer chains (and therefore to have high V_f). On the other hand, PEO (*MW* 18 500) molecules are long enough to behave as random coils, and this increases the free volume. The minimum *MW* for PEO to behave as random coils in solution is 5000[30]. It was also suggested by Papke *et al.* that the minimum *MW* for PEO chains to fold in the crystalline PEO–NaX complex was 6000[27].

Tsushida *et al.*[28] studied PMMA–PEO(*MW* 400)–$LiClO_4$ systems with PEO of *MW*s 6000 and 20 000, and suggested that the formation of a conduction column depended on high-*MW* PEO, but that the number of carrier ions is dominated by low-*MW* PEO. That suggestion might be applied in this case. Here the $8 + 1 + 1$ system has enough low-*MW* PEG to soften the film and molecularly dissolve the salt, and also has a high enough content of PEO (*MW* 18 500) to enhance ionic conduction by itself.

Both PEOs, with *MW*s of 600 and 18 500, can be used as plasticizers in polymer electrolyte systems, due to their liquid state at room temperature in the presence of KSCN. PEO with a *MW* of 600 is a better plasticizer than PEO with a *MW* of 18 500, i.e. PEO (*MW* 600) can decrease T_g more effectively than PEO (*MW* 18 500). However, PEO (*MW* 18 500) can give free volume to the system, due to its long chain that is more difficult to fold, while PEO (*MW* 600) is unable to do so, due to its short oligomeric chain. At a temperature higher than T_g, the free volume of a mixed three-*MW* system is suggested to be higher than those of either of the two-*MW* systems.

CONCLUSIONS

From the results obtained in this work, the following can be concluded:

(1) At low salt concentrations, increasing the salt concentration increases conductivity because of a higher number of free carrier ions. At high concentrations, conductivity decreases because a crystalline complex of PEO and salt is formed, and the 8/1 film is almost completely amorphous. This composition is in the crystallinity gap in the phase diagram.

(2) Mixed salts and mixed anions can increase the conductivity of the system. This might be because of a higher degree of salt dissociation and a higher configurational entropy or disorder in the systems.

(3) Low-*MW* PEO increases conductivity because low-*MW* PEO has a higher content of hydroxyl groups; this group is polar and can enhance salt dissociation into free ions.

(4) Mixing moderate-*MW* PEO with a mixture of high- and low-*MW* PEO enhanced conductivity. This behaviour is attributed to an optimization of the effects of free volume (favoured by the 18 500 *MW* material) and of salt solubilization (favoured by the 600 *MW* material).

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