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CONDUCTIVITIES OF POLY(ETHYLENE OXIDE) AND POLY(2-VINYL PYRIDINE) BLEND

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ABSTRACT

Poly(ethylene oxide) (MW 20,000) and poly(2-vinyl pyridine) (MW 35,000) were blended with $LiClO_4$ or KSCN through a solution blending process. When the molar ratio of ethylene oxide/Li or K is 10, the blend of poly(ethylene oxide)(80 wt%)/poly(2-vinyl pyridine)(20 wt%) with $LiClO_4$ or KSCN is a transparent elastomer. The ionic conductivities of these blends are 1.5×10^{-5} and 8.8×10^{-5} S/cm at 25°C, respectively. At 30°C the poly(ethylene oxide)(80 wt%)/poly(2-vinyl pyridine)(20 wt%) blends with KSCN at an ethylene oxide/K molar ratio of 10 exhibit an ionic conductivity value of 1.5×10^{-4} S/cm, a high value for ionic conductive polymers. At an ethylene oxide/Li molar ratio of 15 and a 2-vinyl pyridine/TCNQ molar ratio of 2, the mixed (ionic-electronic) conductivities of poly(ethylene oxide)(80 wt%)/poly(2-vinyl pyridine)(20 wt%) blends are higher than either ionic or electronic conductivities. When the molar ratio of ethylene oxide/Li and 2-vinyl pyridine/TCNQ are 10 and 2, respectively, the mixed (ionic-electronic) conductivities are intermediate between the ionic and electronic conductivities. Differential scanning calorimetry (DSC) shows that $LiClO_4$ and TCNQ can compatibilize with the PEO/P2VP blend.

INTRODUCTION

Due to extensive studies by Wright et al. [1-3] and Armand et al. [4], knowledge of solid polymer electrolytes has quickly advanced. For most potential applications, such as solid-state batteries, smart windows, and sensors, it is desirable that solid polymer electrolytes display reasonable conductivities, dimensional stability, and processibility at ambient temperature. The main disadvantage of using high molecular weight poly(ethylene oxide) (PEO) is its low ionic conductivities and poor mechanical properties (brittle) at room temperature. Hence, recent research has focused on the use of PEO-containing block copolymers [5, 6], graft copolymers [7, 8], and crosslinked polymers [9] in order to increase both the room temperature conductivities and mechanical properties. However, their preparation requires complicated synthesis and purification processes. Therefore, it is of interest to develop easier methods for the preparation of solid polymer electrolytes with reasonable ionic conductivities, dimensional stabilities, and mechanical properties. Tsuchida et al. [10] reported that the room temperature ionic conductivity for a blend of high molecular weight poly(methacrylic acid) and PEO (MW 6000) was 1.2×10^{-7} S/cm. Li and Khan [11, 12] examined PEO(MW 600,000)/poly(2-vinyl pyridine)(P2VP)(MW 200,000) and poly(4-vinyl pyridine)(P4VP)(MW 50,000) blend systems with $LiClO_4$. The ionic conductivity reached 1.0×10^{-5} S/cm at 25°C for the PEO(85 wt%)/P2VP(15 wt%)/$LiClO_4$ blend when the molar ratio of EO/Li was 10. They also indicated that the $LiClO_4$ salt could compatibilize the PEO and the P2VP by the simultaneous interaction of the lithium ion with oxygen of the PEO and nitrogen of the pyridyl units.

It is well known that poly(2-vinyl pyridine) can complex with TCNQ to form a charge transfer complex and show electrical conductivity [13]. The formation of such a complex is due to electronic interaction between two molecules, one of which is an electron acceptor such as TCNQ and the other is an electron donor. If a blend of poly(2-vinyl pyridine)/poly(ethylene oxide) is doped with $LiClO_4$ and TCNQ, it will show a mixed (ionic-electronic) conductivity. Li and Khan [14] reported that a mixed (ionic-electronic) conductivity of poly(2,5,8,11,14,17,20,23-octaoxapentacosyl methacrylate)-*block*-poly(4-vinyl pyridine) was intermediate between the ionic and electronic conductivities. We reported the synthesis of poly(2-vinyl pyridine)-*graft*-poly(ethylene oxide) [15] with a well-defined structure, and indicated that the graft copolymer, after doping with $LiClO_4$ and TCNQ, showed a mixed conductivity with a synergistic effect which reached 4.4×10^{-5} S/cm at room temperature. However, the preparation of these copolymers is also complicated. This paper deals with the ionic conductivity, electronic conductivity, and mixed (ionic-electronic) conductivity of the PEO/P2VP blend system complexed with both $LiClO_4$ and TCNQ.

EXPERIMENTAL

Preparation of Blends

Poly(ethylene oxide) (MW 20,000) (Japan) was used as received. Poly(2-vinyl pyridine) was synthesized by anionic polymerization of purified 2-vinyl pyridine using potassium naphthalene as initiator. Its molecular weight was determined with a Knauer VPO apparatus, using chloroform as solvent. $LiClO_4$ was an analytical-grade reagent, and it was dried at 160°C before used. KSCN was an analytical-grade reagent. 7,7,8,8-Tetracyano-1,4-quinodimethane (TCNQ) was synthesized according to the literature [16]. Blends of poly(ethylene oxide), poly(2-vinyl pyridine), and $LiClO_4$ or KSCN were prepared by dissolving PEO and P2VP in CH_2Cl_2 followed by the addition of a methanolic solution of $LiClO_4$ or KSCN with stirring for 3.5 hours at room temperature. Blends of PEO, P2VP, and TCNQ were obtained by mixing PEO, P2VP, and TCNQ in DMF and stirring for 5 hours with slight heating. Blends of PEO, P2VP, TCNQ, and $LiClO_4$ were prepared by dissolving PEO/P2VP/$LiClO_4$ blends and TCNQ in DMF and stirring for 5 hours with slight heating. After evaporating the solvents, all the blends were thoroughly dried in a vacuum oven at 60°C for 24 hours.

Measurement of Conductivities

The blend was hot-pressed in a die into a pellet (about 2 mm thick and 14 mm in diameter), sandwiched between two thin aluminum disks at 60°C for the PEO/P2VP/$LiClO_4$ or KSCN blend, 80°C for the PEO/P2VP/$LiClO_4$/TCNQ blend, and 120°C for the PEO/P2VP/TCNQ blend. All the pellets were thoroughly dried over fresh P_2O_5 before measurements were made.

Alternating current conductivities were measured at different temperatures with a DDS-11 conductometer using copper disk electrodes operated at a frequency of 1100–1200 Hz. The determination from 5 to 80°C was repeated once more. There was usually no further reduction in conductivity at room temperature.

DSC

DSC measurements were performed on a Perkin-Elmer DSC-2C Differential Scanning Calorimeter. The samples were first heated from room temperature to 200°C and maintained there for 2 minutes, then the samples were quench cooled at a rate of 320°C/min to −70°C before thermograms were taken. The scanning rate was 10°C/min. The glass transition temperatures (T_g) were taken at the midpoints of the heat capacity changes, and the melting temperatures (T_m) were taken at the maximum of the enthalpy endothermic peaks.

RESULTS AND DISCUSSION

PEO/P2VP/$LiClO_4$ Blend System

When no $LiClO_4$ salt was added to the PEO(80 wt%)/P2VP(20 wt%) blend, this blend appeared to have separated macrophases. After adding $LiClO_4$ salt, this blend showed a different appearance, as indicated in Table 1. When the concentra-

TABLE 1. Appearance of PEO(80 wt%)/P2VP(20 wt%)/ $LiClO_4$ or KSCN Blend System

Molar ratio of EO/Li or EO/K			
5	10	15	20
Opaque Elastomeric	Transparent Elastomeric	Semitransparent Harder	Opaque Phase-separated

tion of the $LiClO_4$ salt is lower (EO/Li = 20), the blend still shows a little phase separation and the blend is not transparent. As the concentration of $LiClO_4$ salt increases, the blend changes into a semitransparent material at EO/Li of 15. When the molar ratio of EO/Li is 10, this blend becomes a transparent elastomer, but when the concentration of $LiClO_4$ salt continues to increase, this blend appears to be an opaque elastomer. These changes can be explained as follows: Lithium ion can interact with the oxygen atom of the PEO and the nitrogen atom of the P2VP due to ion-dipole interactions. The complexing ability of PEO is superior to that of P2VP due to differences in the electronegativity between oxygen and nitrogen and in the steric hindrance of PEO and P2VP. A lithium ion first interacts with the oxygen of PEO when the concentration of lithium ion is lower, hence PEO and P2VP exist as two separate phases, resulting in an opaque and phase-separated appearance. With an increase in the lithium ion concentration, part of the lithium ion can act as a compatibilizer so that the lithium ions can interact with the oxygen of PEO and the nitrogen of P2VP simultaneously. Optical transparency is one of the important criteria [17] used to illustrate the compatibility of two phases. Here, when the molar ratio of EO/Li is 10, the blend appears transparent and elastomeric. This shows that PEO and P2VP are compatible in the presence of a certain amount of lithium ion. However, the PEO/P2VP blend becomes opaque again if the concentration of $LiClO_4$ salt increases further.

The PEO/P2VP/$LiClO_4$ blend can show ionic conductivity. Its Arrhenius conductivity plots are shown in Fig. 1. Some typical conductivities were listed in Table 2. At temperatures lower than or equal to room temperature, maximum values exist when the molar ratio of EO/Li is 10. We also found this phenomenon occurring in the graft copolymer of P2VP-*graft*-PEO [15] we synthesized. Because pyridyl group can consume a part of the $LiClO_4$ salt through ion-dipole interactions, this molar ratio of EO/Li is lower than that in the general PEO/$LiClO_4$ system in which the optimum molar ratio of EO/Li is 20. At 60°C, the maximum conductivity value of PEO/P2VP/$LiClO_4$ occurs when the molar ratio of EO/Li is 15. It is possible that at higher temperatures some ion-dipole interactions between lithium ion and nitrogen may be destroyed, so the free lithium ions may interact with some free oxygen atoms of PEO.

In order to verify the ion-dipole interaction between lithium ions and nitrogen atoms, a blend of P2VP and $LiClO_4$ was made in benzene. After evaporating the solvent and thoroughly drying with P_2O_5, we measured the conductivities of the P2VP/$LiClO_4$ blend. If this blend is conductive, interaction between lithium ion and nitrogen exists. The Arrhenius conductivity plot of P2VP/$LiClO_4$ at a 2VP/Li molar ratio of 10 is presented in Fig. 2. The conductivities from 10 to 100°C are constant and equal to 1.0×10^{-7} S/cm. From 100°C to 135°C the conductivities

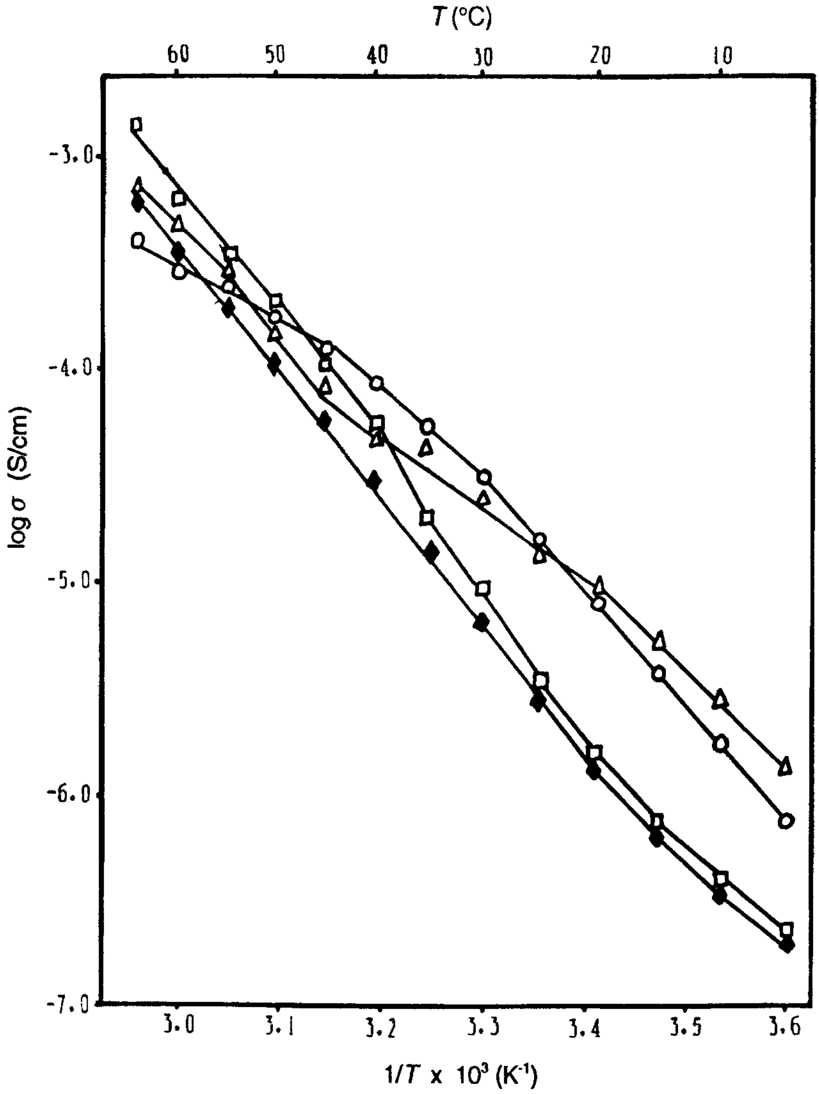

FIG. 1. Arrhenius conductivity plots of PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$ blends: (○) EO/Li = 5, (Δ) EO/Li = 10, (□) EO/Li = 15, and (♦) EO/Li = 20.

increase quickly. This is because the glass transition temperature of P2VP is 104°C [18]. Only when the temperature is high enough can P2VP segments move and cause larger ionic mobility.

PEO/P2VP/KSCN Blend System

PEO and P2VP can also complex with potassium ion to show ionic conductivity. The appearance of PEO(80 wt%)/P2VP(20 wt%) blends with different KSCN concentrations was almost the same as that with different $LiClO_4$ concentrations as

TABLE 2. Conductivities of PEO(80 wt%)/P2VP(20 wt%)/ $LiClO_4$/TCNQ Blend System

	Molar ratio EO/Li	Molar ratio 2VP/TCNQ	$\sigma \times 10^6$ S/cm		
			5°C	25°C	60°C
$LiClO_4$	20	–	0.19	2.9	330
$LiClO_4$	15	–	0.20	3.3	600
$LiClO_4$	10	–	1.4	15	480
$LiClO_4$	5	–	0.75	15	320
TCNQ	–	2	0.15	0.16	3.1
$LiClO_4$,TCNQ	20	2	0.85	7.4	320
$LiClO_4$,TCNQ	15	2	0.27	5.7	690
$LiClO_4$,TCNQ	10	2	0.76	9.4	460
$LiClO_4$,TCNQ	5	2	1.05	6.3	45

shown in Table 1. This indicates that ion–dipole interactions also exist between potassium ion and nitrogen.

Arrhenius plots of the conductivities of PEO/P2VP/KSCN are presented in Fig. 3, and some typical conductivities are listed in Table 3. At lower temperatures the maximum conductivity value occurs when the molar ratio of EO/K is 10. This is also the same as that of PEO/P2VP/$LiClO_4$. Table 3 indicates that the room temperature ionic conductivities of the blends are higher than 1.0×10^{-5} S/cm over all the salt concentration range studied. The ionic conductivity of the PEO/P2VP/KSCN blend at a EO/K molar ratio of 10 is 8.8×10^{-5} S/cm at 25°C and 1.5×10^{-4} S/cm at 30°C, a high value for ionic conductive solid polymers.

Compared with the PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$ blend, the ionic conductivity of the PEO(80 wt%)/P2VP(20 wt%)/KSCN blend is higher. This is because the lattice energy of KSCN is lower than that of $LiClO_4$ [19], and ionic conductivity increases with a decrease in the lattice energy of a salt. Xie [6] showed that the conductivity of PEO complexes decreases in the following order: KSCN > $LiClO_4$.

Electronic Conductivities of PEO/P2VP/TCNQ Blend System

TCNQ can complex with P2VP to form a charge transfer complex. When the PEO(80 wt%)/P2VP(20 wt%) blend was doped with TCNQ, the Arrhenius conductivities of the blends plotted in Fig. 4 resulted. In the temperature range studied, conductivity increases with the concentration of TCNQ doped in the PEO/P2VP blend. This is because more carriers are formed in the blend with higher TCNQ concentrations.

When the PEO/P2VP blend is doped with TCNQ, TCNQ can also form charge transfer complex with the oxygen of PEO because oxygen has a lone pair of electrons and acts as an electron donor. Therefore, electronic conductivity is contributed to complexes of TCNQ with the nitrogen of P2VP and the oxygen of PEO.

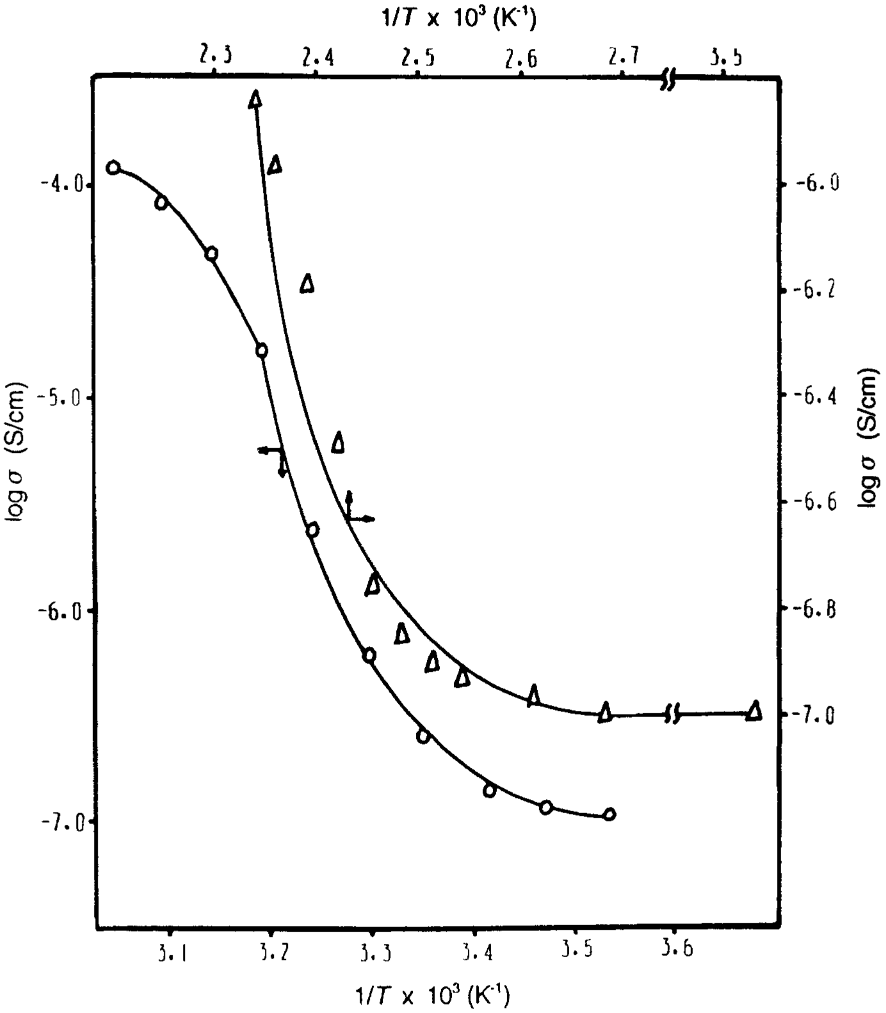

FIG. 2. Arrhenius conductivity plots of PEO/TCNQ and P2VP/LiClO$_4$ complexes: (○) EO/TCNQ = 10 and (△) 2VP/Li = 10.

The Arrhenius plot of conductivities of the PEO/TCNQ complex with an EO/TCNQ molar ratio of 10 are also shown in Fig. 2. The conductivity increases with increasing temperature. At temperatures higher than 30°C the conductivity increases more quickly than at temperatures lower than 30°C. This is because the crystalline phase of PEO begins to melt into an amorphous phase at temperatures higher than 30°C. The hard crystalline PEO chains change into soft amorphous PEO chains which make the carriers easy to merge, resulting in a fast increase of conductivity with rising temperature.

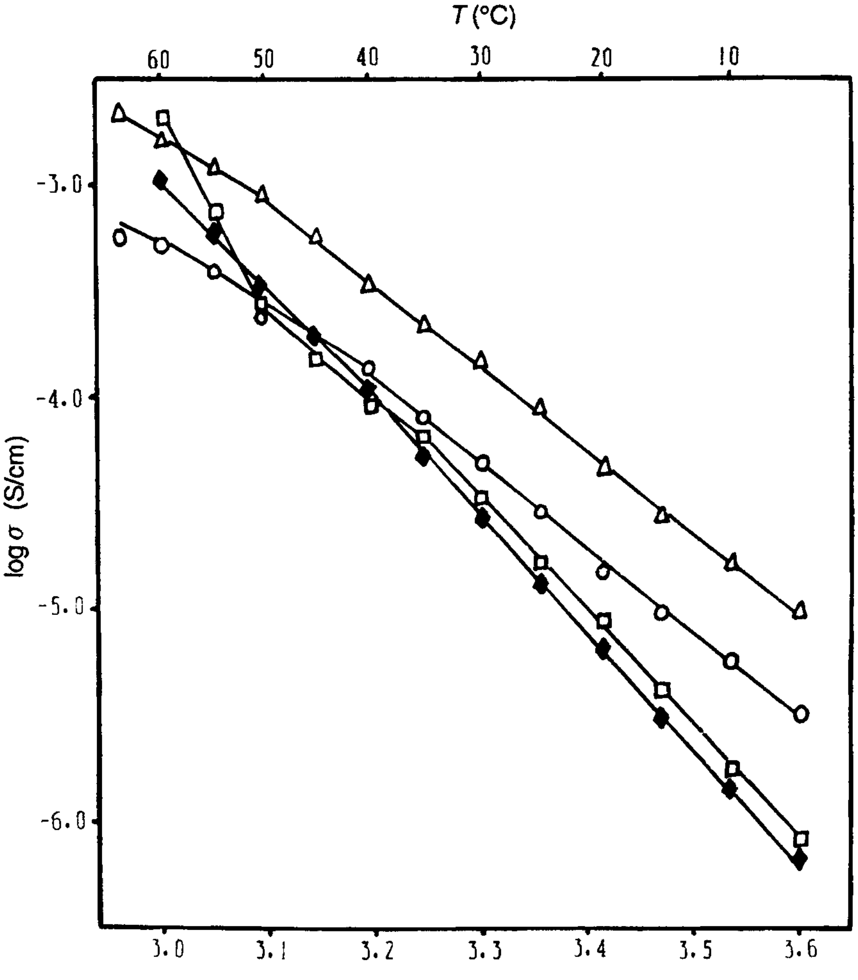

FIG. 3. Arrhenius conductivity plots of PEO(80 wt%)/P2VP(20 wt%)/KSCN blends: (○) EO/K = 5, (△) EO/K = 10, (□) EO/K = 15, and (♦) EO/K = 20.

Mixed (Ionic-Electronic) Conductivity of PEO/P2VP/LiClO$_4$/TCNQ Blend System

Figure 5 illustrates the mixed (ionic-electronic) conductivity of the PEO(80 wt%)/P2VP(20 wt%)/LiClO$_4$/TCNQ blend system. The molar ratio of 2VP/TCNQ in all four plots of Fig. 5 was 2. At 25°C the mixed (ionic-electronic) conductivities of the blend are greater than 3.5×10^{-6} S/cm, as indicated in Table 2. The highest mixed conductivity at 25°C occurs when the molar ratio of EO/Li is 10, and at 60°C the highest conductivity occurs at an EO/Li molar ratio of 15. These are the same as those in the PEO(80 wt%)/P2VP(20 wt%)/LiClO$_4$ blend system.

TABLE 3. Conductivities of PEO(80 wt%)/P2VP(20 wt%)/KSCN Blend System

Molar ratio EO/K	$\sigma \times 10^6$ S/cm		
	5°C	25°C	60°C
20	0.70	14	940
15	0.76	16	2000
10	9.5	88	1600
5	3.2	29	520

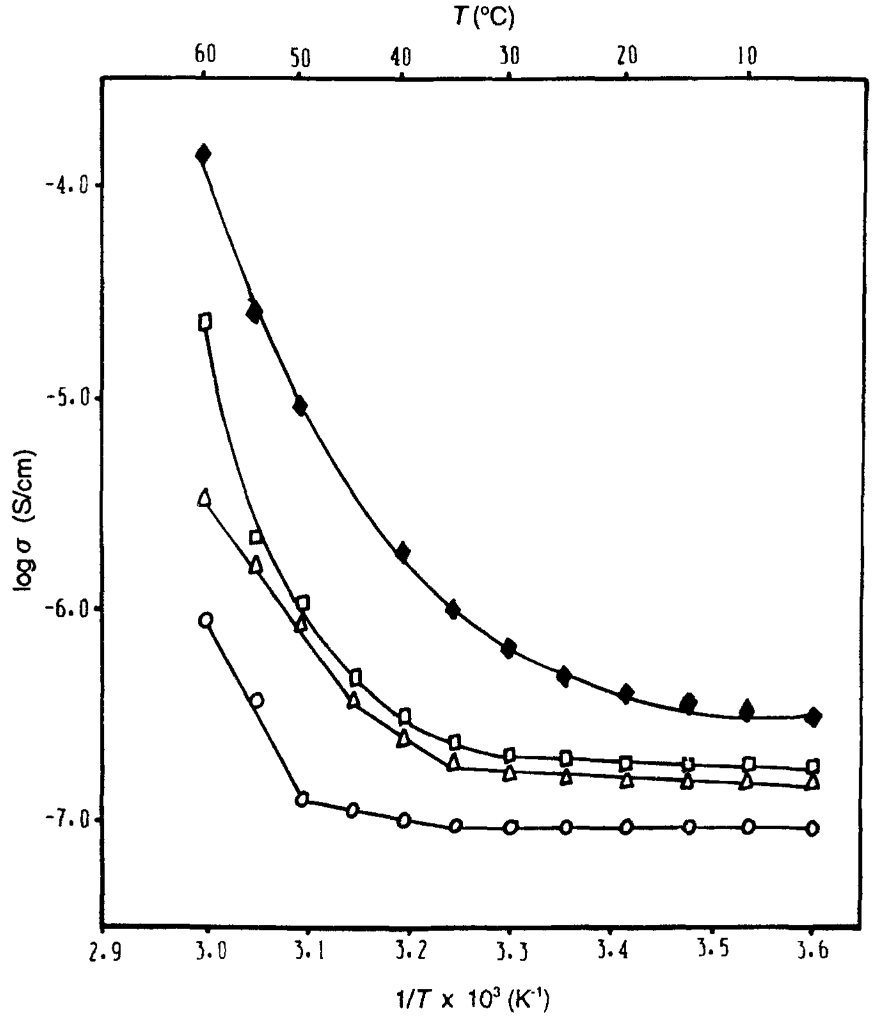

FIG. 4. Arrhenius conductivity plots of PEO(80 wt%)/P2VP(20 wt%)/TCNQ blends: (○) TCNQ/2VP = 0.2, (△) TCNQ/2VP = 0.5, (□) TCNQ/2VP = 1.0, and (♦) TCNQ/2VP = 1.3.

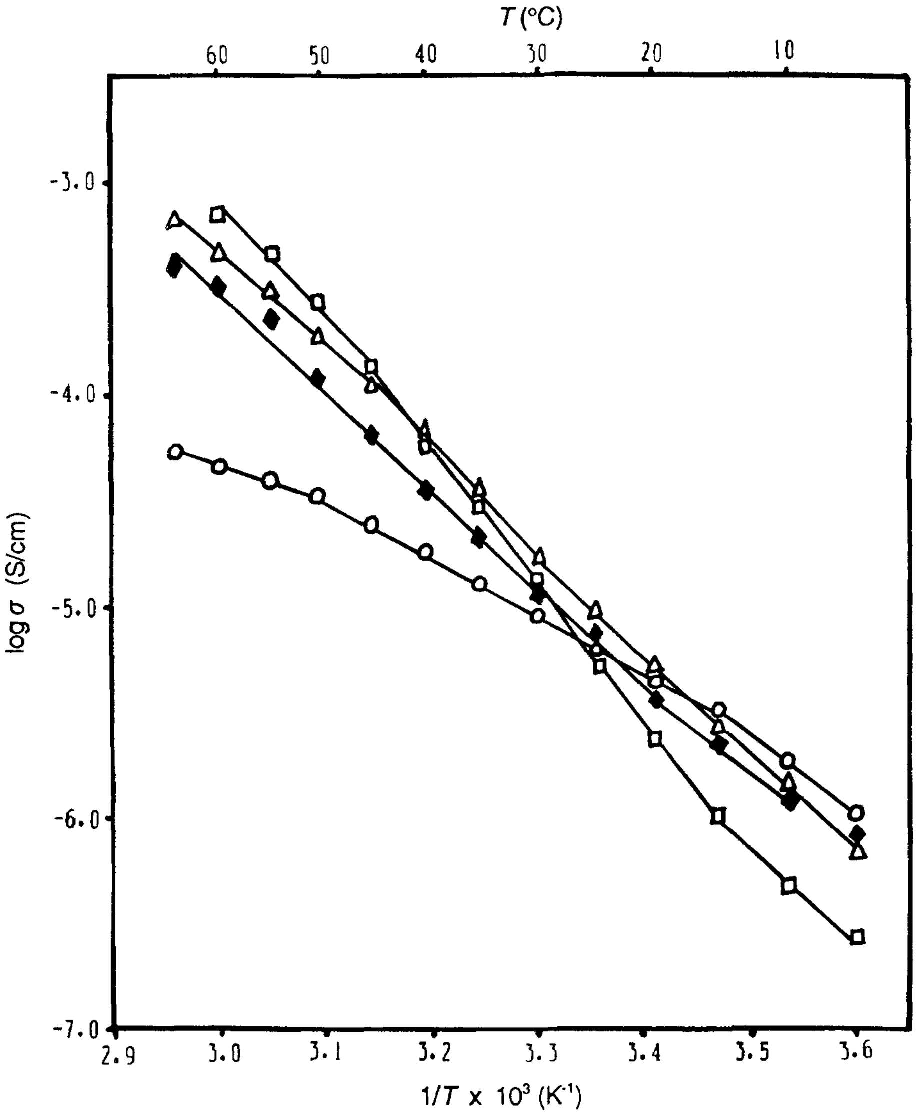

FIG. 5. Arrhenius conductivity plots of PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$/TCNQ blends: TCNQ/2VP = 0.5, (○) EO/Li = 5, (△) EO/Li = 10, (□) EO/Li = 15, and (♦) EO/Li = 20.

When the molar ratios of EO/Li and 2VP/TCNQ are 15 and 2, respectively, the mixed (ionic-electronic) conductivities are higher than the ionic conductivities of the PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$ blend and the electronic conductivities of the PEO(80 wt%)/P2VP(20 wt%)/TCNQ blend in the temperature range studied. We also found a synergistic effect of mixed conductivity in P2VP-*graft*-PEO [15]. When the molar ratios of EO/Li and 2VP/TCNQ are 10 and 2, respectively, the mixed (ionic-electronic) conductivities are intermediate between the ionic

TABLE 4. Glass Transition Temperatures (T_g), Melting Temperatures (T_m), and Heat of Fusion (ΔH) of PEO, PEO(80 wt%)/P2VP(20 wt%)/ $LiClO_4$(KSCN) or TCNQ Blend

EO/Li (molar ratio)	TCNQ/2VP (molar ratio)	T_g, °C	T_m, °C	ΔH, cal/g
–[a]	–	–	65.8	30.8
20	–	−46.8	58.8	18.1
10	–	−33.6		
5	–	−23.4		
–	0.2	–	62.8	22.5
–	0.5	−30.9	55.9	18.5
10[b]	–	−42.9		
PEO		–	72.7	36.5

[a] PEO/P2VP blend without $LiClO_4$ or TCNQ.

[b] PEO/P2VP/KSNC blend at an EO/K molar ratio of 10.

and electronic conductivities. How the ionic and electronic conductivities contribute to the mixed conductivities is not yet known and needs further study.

It is expected that with a change of the molar ratio of EO/Li or 2VP/TCNQ, different magnitudes of mixed (ionic-electronic) conductivities can be obtained to fit different applications.

DSC

Table 4 lists the T_g, T_m, and heat of fusion (ΔH) of PEO and the PEO/P2VP blend doped with $LiClO_4$, KSCN, and TCNQ. For PEO and the PEO/P2VP blend, no T_g were measured; perhaps the T_g of PEO is lower. Table 4 shows that T_g of the PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$ blend increases with decreasing EO/Li molar ratio, and no T_m and ΔH can be observed with EO/Li $\leq$ 10. This can be explained by the fact that more complexes are formed between PEO, P2VP, and Li^+ in the blend, and the crystalline phase of PEO was changed into an amorphous phase of PEO. T_m and ΔH of the PEO/P2VP/$LiClO_4$ blend at an EO/Li molar ratio of 20 are also lower than those of PEO or the PEO/P2VP blend, which indicates that PEO and P2VP can be compatibilized by $LiClO_4$ salt because T_m of the crystalline phase in the blend shows miscibility between two different parts in the blend [17]. At an EO/K molar ratio of 10, T_g of the PEO/P2VP/KSCN blend is −42.9°C, which is lower than that of the PEO/P2VP/$LiClO_4$ blend at the same molar ratio; no crystalline fusion peak was observed. This may be due to the larger radius of K^+ than of Li^+, resulting in more interference with the crystalline phase of PEO.

In the study of PEO/P2VP/TCNQ blends we found that TCNQ can also compatibilize the PEO/P2VP blend because TCNQ is an electron acceptor and

PEO or P2VP has an oxygen atom or a nitrogen atom with a lone pair of electrons. When the molar ratio of TCNQ/2VP is 0.2 or 0.5, a PEO/P2VP/TCNQ casting from DMF solution is a piece of glossy film. With an increasing TCNQ/2VP molar ratio, T_m and ΔH decrease, which implies that the crystalline phase of PEO decreases. T_g increases to −30.9°C at a molar ratio of 0.5, as shown in Table 4. This may contribute to the charge transfer complexes formed between TCNQ and P2VP or between TCNQ and PEO. When the molar ratio of TCNQ/2VP is 1.0 or 1.3, the PEO/P2VP/TCNQ blend cannot form a film.

CONCLUSION

PEO(80 wt%)/P2VP(20 wt%)/$LiClO_4$ or KSCN was a transparent elastomer at an EO/Li or EO/K molar ratio of 10. The ionic conductivity of PEO/P2VP/$LiClO_4$ or KSCN reaches 1.5×10^{-5} and 8.8×10^{-5} S/cm, respectively, with an EO/Li or EO/K molar ratio of 10 at 25°C. For PEO/P2VP/KSCN, the conductivity reaches 1.5×10^{-4} S/cm at 30°C. After being complexed with TCNQ, the PEO/P2VP/$LiClO_4$ blend exhibits mixed (ionic-electronic) conductivity. When the molar ratios of EO/Li and 2VP/TCNQ are 15 and 2, respectively, the mixed (ionic-electronic) conductivities are higher than the ionic or electronic conductivities in the temperature range studied. T_g of the PEO/P2VP/$LiClO_4$ blend increases with increasing $LiClO_4$ salt in the range studied. The T_m and heat of fusion of the PEO/P2VP blend can also be lowered by adding $LiClO_4$ or TCNQ.

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