Highly Conductive Solid Polymer Electrolytes Prepared by Blending High Molecular Weight Poly(ethylene oxide), Poly(2- or 4-vinylpyridine), and Lithium Perchlorate

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ABSTRACT: Highly ionic conductive solid polymer electrolytes have been prepared by blending poly(ethylene oxide) (MW 600 000) and poly(2-vinylpyridine) (MW 200 000) or poly(4-vinylpyridine) (MW 50 000) and $LiClO_4$. All blends were prepared by the solution blending process. Several different blend compositions have been studied and optimum compositions required for preparing solid polymer electrolytes have been determined. The poly(ethylene oxide) (85% by weight)/poly(2-vinylpyridine) (15% by weight)/$LiClO_4$ blend at an ethylene oxide/Li^+ mole ratio of 10 exhibits an ionic conductivity value of 1.0×10^{-5} S cm^{-1} at 25 °C and is an elastomeric material with dimensional stability. Furthermore, this blend exhibits ionic conductivities $>3.0 \times 10^{-6}$ S cm^{-1} at 25 °C over a wide salt concentration range. Several other blends prepared are also elastomeric materials with ionic conductivities $\sim 5.0 \times 10^{-6}$ S cm^{-1}, e.g. poly(ethylene oxide) (85% by weight)/poly(2-vinylpyridine) (15% by weight)/$LiClO_4$ at an ethylene oxide to Li^+ mole ratio of 6 exhibits a value of 7.0×10^{-6} S cm^{-1} at 30 °C. Studies indicate that the $LiClO_4$ salt compatibilizes the poly(ethylene oxide) and the poly(2-vinylpyridine) by the simultaneous interaction of the Li^+ with the oxygens of the PEO and nitrogen of the pyridyl units. Scanning electron microscopy (SEM) on the internal structure of the blends shows the presence of a two phase microstructure, most likely, stabilized by the emulsifying effect of $LiClO_4$.

Introduction

We have recently reported that blends of commercially available poly(ethylene oxide) (MW 600 000)/poly(2-vinylpyridine) (MW 200 000) at weight ratios of 3 to 1, respectively, and containing different $LiClO_4$ concentrations are solid elastomeric materials with ionic conductivities as high as 6.0×10^{-6} S cm^{-1} at 30 °C.[1] These properties make the blends attractive materials for potential use as solid polymer electrolytes in microelectronic devices. The field of solid polymer electrolytes or ionic conductive polymers has quickly advanced because of the insightful studies of Wright et al. and Armand and co-workers.[2-5] Applications of solid polymer electrolytes include solid state batteries, smart windows, components in solid state sensors, and solid state transistors.[3-12] For most potential applications, it is desirable that the solid polymer electrolytes display reasonable conductivities ($\sim 10^{-5}$ S cm^{-1}), dimensional stability, and elastomeric properties at room temperature.[4,5] Poly(ethylene oxide)/alkali metal salt complexes exhibit interesting electrical properties, but their low ionic conductivities and poor mechanical properties (brittle) preclude room temperature application.[4,13] Furthermore, at a higher temperature (~100 °C) poly(ethylene oxide)/alkali metal salt complexes are a viscous tacky material susceptible to undergoing creep.[14] Because of the inherent drawbacks of poly(ethylene oxide)/alkali metal salt complexes, numerous new polymer/salt electrolyte systems have been developed. For example, poly(siloxane) or poly(phosphazene) with pendant oligo(oxyethylene) side chain/salt electrolyte systems exhibit ionic conductivities greater than 10^{-5} S cm^{-1} at room temperature.[15,16] However, these liquidlike polymer electrolytes must be cross-linked or blended with high molecular weight poly(ethylene oxide) or other polymers to obtain materials with dimensional stability.[15,17,18] Dimensionally stable polymer electrolytes have been prepared by using block copolymers where the low T_g ionic conductive block is reinforced by a high T_g nonconductive block.[19-22] While a large number of new polymer/salt complexes are promising materials, the fact that their preparation requires nontrivial synthetic, cross-linking or blending processes is a serious drawback. Therefore, it is of considerable interest to develop easier methodologies for preparing solid polymer electrolytes with reasonable ionic conductivities, dimensional stability, and elastomeric properties.[23] In this regard, our recent report on the preparation of solid polymer electrolytes by blending commercial polymers is of interest.[1]

In addition to our work, a few other groups have also utilized the technique of blending to prepare solid polymer electrolytes.[1,14,24,25] Tsuchida et al. have examined blends of high molecular weight poly(methacrylic acid) and low molecular (400 and 6000) poly(ethylene oxide). The room temperature ionic conductivity observed for a blend system using poly(ethylene oxide) of molecular weight 6000 was 1.2×10^{-7} S cm^{-1}.[26] Blends of poly(ethylene oxide)/poly(styrene)/$LiCF_3SO_3$ prepared by hot pressing techniques had superior mechanical properties relative to poly(ethylene oxide)/$LiCF_3SO_3$ but the ionic conductivities were lower because of the presence of the nonconductive poly(styrene) phase.[14] The PEO(75 by weight)/P2VP(25 by weight)/$LiClO_4$ blend system exhibits interesting behavior.[1] For example, the ionic conductivity of the blend, in the salt concentration range studied, increased with increasing salt content; whereas the conductivity of the PEO/$LiClO_4$ system initially increases with increasing salt content, reaches a maximum value at an ethylene oxide/Li^+ mole ratio of 10, and decreases as the salt content is further increased. This behavior has been attributed to the effectiveness of poly(2-vinylpyridine) in dispersing the salt throughout the blend, i.e. impeding the formation of the less mobile aggregates. Furthermore, poly(ethylene oxide) and poly(2-vinylpyridine) are immiscible at weight ratios of 3 to 1, respectively, but are compatibilized by $LiClO_4$. The exact mechanism by which $LiClO_4$ compatibilizes the two polymers is not clearly understood, but it is most likely because the Li^+ ion simultaneously interacts with the oxygens of the poly(ethylene oxide) and the

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nitrogen of the pyridine unit. Eisenberg and co-workers have previously demonstrated that similar types of ion-dipole interactions lead to the miscibility enhancement in polystyrene ionomers and poly(alkylene oxide) systems.[27]

In light of these interesting observations, we have started a systematic study to explore the feasibility of blending to prepare solid polymer electrolytes. In this paper we report on the preparation and characterization of a number of poly(ethylene oxide)/poly(2- or 4-vinylpyridine)/$LiClO_4$ blends prepared by the solution blending process.

Experimental Section

Preparation of Blends. Poly(ethylene oxide) (MW 600 000), poly(2-vinylpyridine) (MW 200 000), and poly(4-vinylpyridine) (MW 50 000), obtained from Polysciences, were used as received. The $LiClO_4$ (Aldrich) salt used was dried in a vacuum oven at 50 °C and stored in a desiccator. All the blends were prepared by the same method. For example, blends of poly(ethylene oxide) (PEO), poly(2-vinylpyridine) (P2VP), and $LiClO_4$ were prepared by dissolving PEO and P2VP in CH_2Cl_2 followed by the addition of a solution of $LiClO_4$/THF with vigorous stirring for 3 h at ambient temperature. The solvent was removed by evaporation under a N_2 stream at room temperature. The blends were dried in a vacuum oven for at least 2 days at 50 °C. All samples were stored in a desiccator and dried again overnight in a vacuum oven at 60 °C before conductivity measurements were undertaken. Throughout this report abbreviations have been used to identify different blends. For example, PEO(75)/P4VP(25)/$LiClO_4$ blends at an ethylene oxide to Li^+ mole ratio of 4 indicate a blend containing 75% by weight PEO and 25% by weight P4VP to which sufficient $LiClO_4$ salt has been added.

Measurements. Conductivity measurements were carried out on polymer disks (1.25 cm in diameter) held between copper plates under a dried N_2 stream, using a Hewlett-Packard 4192A impedance analyzer over the range 5 Hz to 13 MHz. Bulk resistance was derived from the Cole–Cole plot of the complex impedance data of the blend where the imaginary impedance is zero.[28-30] Conductivity was calculated from the bulk resistance according to the following equation

$$\sigma = D/A \times R_b$$

where σ is conductivity, D is the thickness of the sample, A is the section area of the sample, and R_b is bulk resistance.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-4 equipped with a thermal data station. The samples were scanned at a heating rate of 20 °C min^{-1}. The samples were first heated to 200 °C and quench cooled at a rate of 320 °C/min to −80 °C before obtaining thermograms. 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. The scanning electron micrographs were obtained on a Hitachi S-800SEM operating at 15 kV. The specimens were prepared by cryogenically fracturing polymer blend films under liquid nitrogen. To reduce charging effects, the specimens were sputter coated with a thin layer of gold.

Results

(A) PEO/P2VP/$LiClO_4$ Blends. In Figure 1, the Arrhenius conductivity plots for the PEO(85)/P2VP(15)/$LiClO_4$ blends with different salt contents are presented. These plots indicate that the ionic conductivity increases as the salt content is increased; it reaches a maximum value at an ethylene oxide/Li^+ mole ratio of 10 and decreases as the salt content is further increased. A plot of log σ versus the ethylene oxide/Li^+ mole ratio for the blend demonstrates this behavior (Figure 2). While this observation is consistent with the generally observed behavior for polymer salt complexes,[5] e.g. poly(ethylene oxide)/$LiClO_4$, it is in contrast to the PEO(75)/P2VP(25)/$LiClO_4$ blends. It is interesting to note that the ionic conductivity of the PEO(85)/P2VP(15)/$LiClO_4$ blend at an ethylene oxide/Li^+ mole ratio of 10 is 1.0×10^{-5} S cm^{-1} at room temperature, a value which is considered high in the area of ionic conductive solid polymers. Additionally, this blend is an elastomeric material with dimensional stability. Furthermore Figure 2 indicates that the ionic conductivities of the blend are greater than 3.0×10^{-6} S cm^{-1} over the total salt concentration range studied. This is in contrast to the PEO/$LiClO_4$ system. The ionic conductivity of the PEO/$LiClO_4$ system quickly increases with increasing salt content, reaches a maximum, and sharply decreases as the salt content is further increased.[1] Most polymer salt complexes show behavior similar to the PEO/$LiClO_4$ system.[5,15,16] In Figure 3, the DSC thermographs of PEO(85)/P2VP(15)/$LiClO_4$ at different salt contents are shown. At a higher salt content the T_g of the blend increases, this increase is not observed for the blend with 25% poly(2-vinylpyridine) content.[1] In Table I, the thermal and ionic conducting properties of the two PEO/P2VP/$LiClO_4$ blends with 15% and 25% P2VP contents are listed. The ionic conductivity values for the PEO/$LiClO_4$ polymer electrolytes measured by us are in agreement with data determined under similar conditions.[7,31] Howver, it had been shown that the conductivity values of the PEO/$LiClO_4$ system are lower when allowed to crystallize for a long period of time at room temperature.[32,33] Therefore, slow crystallization may be a problem for certain PEO based electrolytes. But the PEO(85)/

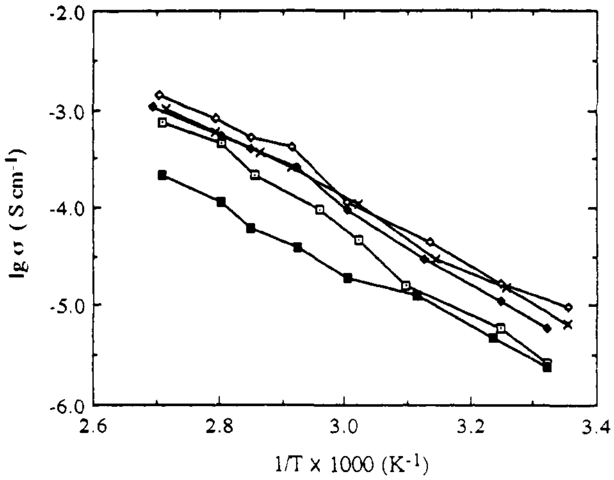


Figure 1. Arrhenius conductivity plots of PEO(85)/P2VP(15)/$LiClO_4$ blends: (■) EO/Li = 5; (◇) EO/Li = 10; (×) EO/Li = 15; (◆) EO/Li = 20; (⊡) EO/Li = 25.

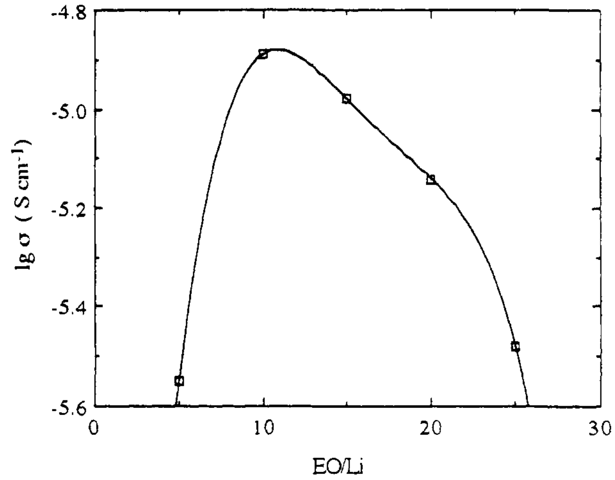


Figure 2. Log σ vs ethylene oxide/Li^+ mole ratio plot for PEO(85)/P2VP(15)/$LiClO_4$ complexes at 30 °C.

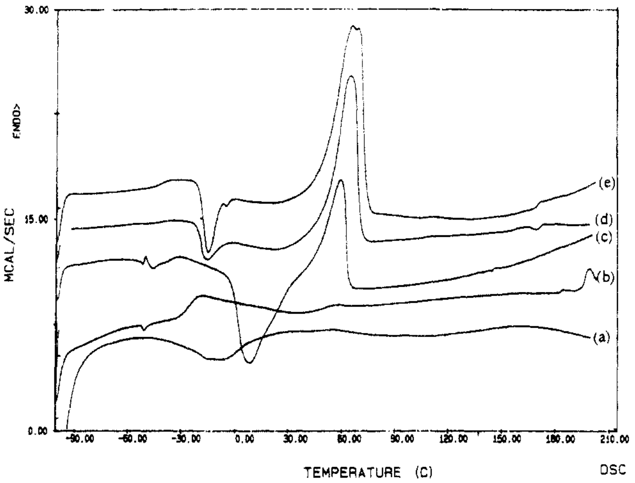


Figure 3. DSC thermographs of PEO(85)/P2VP(15)/LiClO$_4$ complexes: (a) EO/Li = 5; (b) EO/Li = 10; (c) EO/Li = 15; (d) EO/Li = 20; (e) EO/Li = 25.

Table I. Glass Transition Temperature (T_g), Recrystallization Temperature (T_c), Melting Temperature (T_m), and Ionic Conductivity of PEO/P2VP/LiClO$_4$ Complexes

blend (PEO/P2VP)	EO/Li$^+$	T_g (°C)	T_c (°C)	T_m (°C)	σ^a (S cm^{-1})
85%/15% (wt)	5	4			6.3×10^{-6}
	10	−27			1.3×10^{-5}
	15	−39	−10	59	1.1×10^{-5}
	20	−39	14	65	7.6×10^{-6}
	25	−41	15	63	3.6×10^{-6}
75%/25% (wt)^b	2	−48			6.0×10^{-6}
	5	−35			3.6×10^{-6}
	10	−41	10	43	1.1×10^{-6}
	15	−35	20	62	6.5×10^{-7}
	20	−34	6	65	2.0×10^{-7}
	25	−40	−11	66	4.8×10^{-8}

^{a} 30 °C. ^{b} From ref 1.

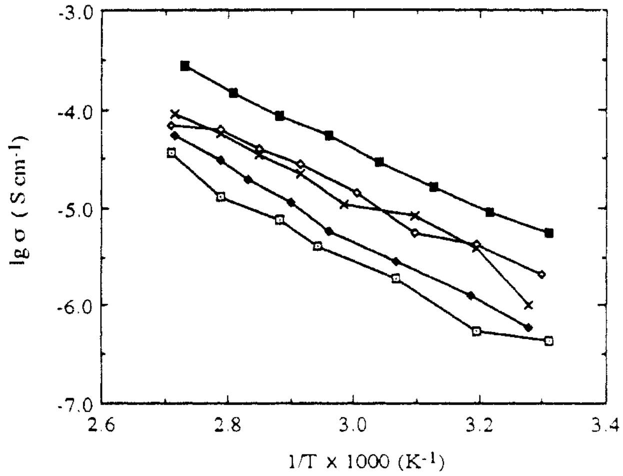


Figure 4. Arrhenius conductivity plots of PEO(75)/P4VP(25)/LiClO$_4$ blends: (■) EO/Li = 2; (◇) EO/Li = 4; (×) EO/Li = 6; (◆) EO/Li = 8; (▣) EO/Li = 10.

P2VP(15)/LiClO$_4$ blend (at a EO/Li$^+$ mole ratio of 10) does not show a loss on the ionic conductivity after the sample was allowed to stand at room temperature for 3 months and heated to 40 °C, below the temperature of the eutectic composition, before measuring conductivity. Thus, within the time frame of the experiment slow crystallization is not a problem for this sample.

(B) PEO/P4VP/LiClO$_4$ Blend. In Figure 4, the Arrhenius conductivity plots of PEO(75)/P4VP(25)/LiClO$_4$ at different salt contents are presented. The data indicate that the ionic conductivity, up to an ethylene oxide/Li$^+$ mole ratio of 2, increases with increasing salt content. This observation is similar to the PEO(75)/P2VP(25)/LiClO$_4$ system.[1] The ionic conductivity of the PEO(75)/P4VP(25)/LiClO$_4$ blend sharply decreases to <1 × 10^{-9} S cm^{-1} at 30 °C as the salt concentration is increased to an ethylene oxide/Li$^+$ mole ratio of 1. Similar behavior is observed for the corresponding P2VP blend. This sudden decrease is possibly the rocklike hard material formed due to the very high salt content in the blend. It was not possible to obtain any meaningful thermal properties of this blend from DSC measurements. The thermal characteristics of the PEO(75)/P4VP(25)/LiClO$_4$ blends are similar to the blend containing 25% of P2VP. Both systems are similar in that the T_g does not increase as the salt content, in the range studied, is increased. However, the T_g of the P4VP(25%) containing blend is approximately 10–15 deg higher than that of the P2VP system. In Table II, the thermal transitions and the ionic conductivities of the PEO/P4VP/LiClO$_4$ blends are listed. The data indicate that the conductivity behavior of the PEO(85)/P4VP(15)/LiClO$_4$ blends is similar to the corresponding PEO(85)/P2VP(15)/LiClO$_4$ blends; i.e. initially, the conductivity increases, reaches a maximum, and decreases as the salt concentration is further increased. The maximum conductivity at 30 °C for the P4VP system is 7.0 × 10^{-6} S cm^{-1} at an ethylene oxide/Li$^+$ mole ratio of 6 compared to the 1.3 × 10^{-5} S cm^{-1} reached at an ethylene oxide/Li$^+$ mole ratio of 10 for the P2VP system. The DSC thermographs of the PEO(85)/P4VP(15)/LiClO$_4$ blends are shown in Figure 5. The thermographs indicate that the glass transition temperature increases at the higher salt contents. Similar behavior is observed for the PEO(85)/P2VP(15)/LiClO$_4$ blends. The PEO(65)/P4VP(35)/LiClO$_4$ blends exhibit a maximum conductivity of 3.3 × 10^{-6} S cm^{-1} at 30 °C at an ethylene oxide/Li$^+$ mole ratio of 6. The ionic conductivities of both the PEO(65)/P4VP(35)/LiClO$_4$ and PEO(75)/P4VP(25)/LiClO$_4$ blends are lower than that for PEO(85)/P4VP(15)/LiClO$_4$. In these blend systems there is a complex interrelationship of the conductivity value with the composition, glass transition, morphology, and salt content.

Table II. Glass Transition Temperature (T_g), Recrystallization Temperature (T_c), Melting Temperature (T_m), and Ionic Conductivity of PEO/P4VP/LiClO$_4$ Complexes

blend (PEO/P4VP)	EO/Li$^+$	T_g (°C)	T_c (°C)	T_m (°C)	σ^a (S cm^{-1})
85%/15% (wt)	2				8.0×10^{-7}
	4	−8.5			2.3×10^{-6}
	6	−14			7.0×10^{-6}
	8	−23	36	53	3.0×10^{-6}
	10	−22	38	64	1.4×10^{-6}
75%/25% (wt)	2				6.0×10^{-6}
	4	−23			1.5×10^{-6}
	6	−17			1.7×10^{-6}
	8	−29	36	56	4.3×10^{-7}
	10	−23	35	80	4.7×10^{-7}
65%/35% (wt)	2				5.4×10^{-9}
	4	−16			1.0×10^{-6}
	6	−15			3.3×10^{-6}
	8	−33	23	55	7.2×10^{-7}
	10	−34	6.4	66	6.3×10^{-7}

^{a} At 30 °C.

Discussion

Belfiore and co-workers have demonstrated that poly(4-vinylpyridine) and poly(ethylene oxide) are immiscible.[34] Their studies have also shown that PEO/P2VP

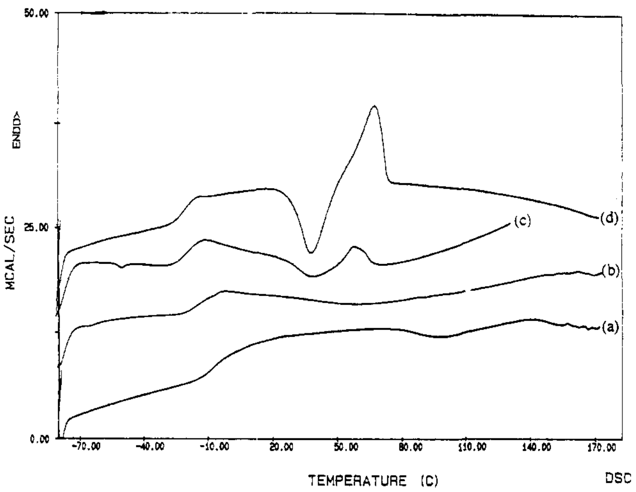
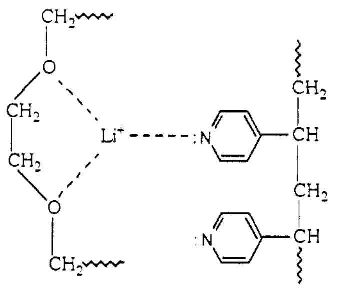


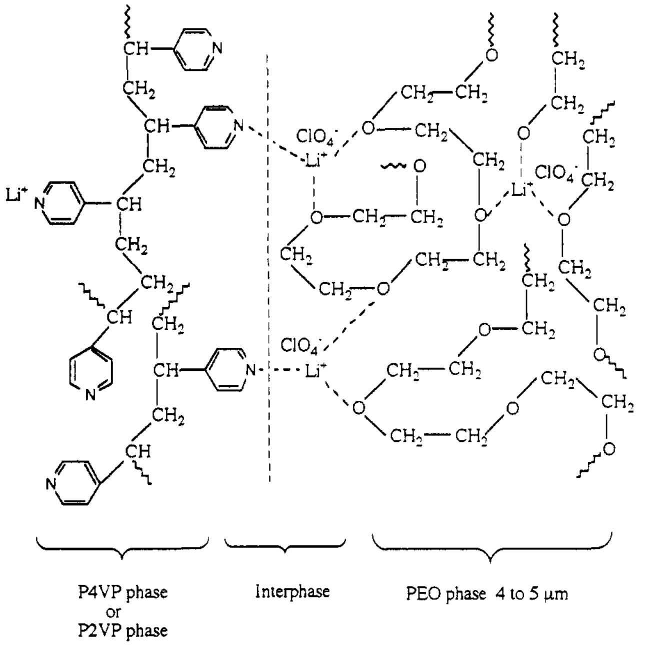
Figure 5. DSC thermographs of PEO(85)/P4VP(15)/$LiClO_4$ complexes: (a) EO/Li = 4; (b) EO/Li = 6; (c) EO/Li = 8; (d) EO/Li = 10.

blends at a composition of 40/60 respectively are only slightly miscible. In the blend composition range of this study, PEO and P2VP are immiscible, as indicated by the independence of both the T_m of PEO and the T_g of P2VP as a function of the composition of the mixture. Therefore, $LiClO_4$ acts as the compatibilizing agent in both the PEO/P2VP and PEO/P4VP blends. We have already reported that the miscibility enhancement in the PEO/P2VP blends is most likely because the lithium ion simultaneously interacts with the oxygens of the PEO and the nitrogen of the 2-pyridyl unit. We believe similar types of ion–dipole interactions, as depicted in I, are responsible for the miscibility or compatibilization of PEO and P4VP. Ion–dipole interactions have been demonstrated to enhance the miscibility of poly(styrene) ionomers with poly(alkylene oxide) systems[27] and polyamide-6 with lithium or sodium sulfonated polystyrene.[35,36] Also, Stevens and co-workers have observed that $LiCF_3SO_3$ enhances the miscibility of poly(methyl methacrylate) and poly(propylene glycol).[8] The miscibility enhancement was rationalized on the basis of the simultaneous interaction of the Li^+ with the carbonyl oxygens of poly(methyl methacrylate) and ether oxygens of poly(propylene glycol). Furthermore, the blends have been shown to have a phase separated structure with $LiCF_3SO_3$ acting as an emulsifier in stabilizing the two phase microstructure.[37]



I

Scanning electron micrographs of the cryogenically fractured internal surface of PEO(75)/P2VP(25)/$LiClO_4$ with different salt contents are shown in Figure 6. As the salt concentration is increased from an ethylene oxide/Li^+ mole ratio of 20 to 5, the texture of the internal surface becomes more homogeneous. The fractured surface with an ethylene oxide/Li^+ mole ratio of 20 shows a crack indicating insufficient cohesive force between the components in the blends. The internal structure, Figure 6c, of the blend with an ethylene oxide/Li^+ mole ratio of 5 shows a smooth surface with partially anisotropic stringlike patterns. The strings in the pattern are approximately 4–5 μm in diameter. The surface with the intermediate salt content is approximately half covered by the partially anisotropic stringlike pattern. In this case sufficient $LiClO_4$ is not available to totally compatibilize the two polymers. Most likely, these partially anisotropic stringlike patterns are poly(ethylene oxide)/$LiClO_4$ domains in a matrix of poly(2-vinylpyridine). The $LiClO_4$ acts as an emulsifier to stabilize the two phases. Because these poly(ethylene oxide) phases are only 4–5 μm in diameter, formation of well defined PEO crystallites is not probable and hence a mostly amorphous PEO phase is formed. The scanning electron micrographs of PEO(75)/P4VP(25)/$LiClO_4$ show a similar type of trend (Figure 7): increasing the salt content, increasing the stringlike pattern. Again, the strings are possibly the PEO phase immersed in a P4VP phase with the $LiClO_4$ acting as an emulsifying agent. The emulsifying effect of $LiClO_4$ is depicted in II. The $LiClO_4$ salt is present both in the pure PEO phase and pure P4VP or P2VP phase, but it is the $LiClO_4$ at the interphase that stabilizes the two phase microstructure by ion–dipole interactions. These arguments are consistent with the SEM and DSC results. Furthermore, the arguments are similar to those used by Stevens and co-workers for explaining the miscibility enhancement of poly(methyl methacrylate) and poly(propylene glycol) by $LiCF_3SO_3$.[8,37] By DSC we are clearly able to observe the T_g of the amorphous PEO phase in the blend but the T_g for the poly(vinylpyridine) is not observed. One of the reasons for this may be that the poly(2- or 4-vinylpyridine) domain size is too small and not discernible by DSC, but a more probable reason is that poly(2- or 4-vinylpyridine) complexed with $LiClO_4$ through the lone pair electron of the nitrogen atom has a completely different T_g. DSC studies on poly(2- or 4-vinylpyridine) with high contents (vinylpyridine to $LiClO_4$ mole ratio ≥ 10) did not show any glass transitions up to 200 °C. Complexation of poly(2- or 4-vinylpyridine) with $LiClO_4$ results in a rigid polymer matrix with little segmental motion. However, at lower $LiClO_4$ contents, the T_g of the poly(2-vinylpyridine)/$LiClO_4$ system increases with increasing salt concentration. For example, the T_g's at vinylpyridine to



II

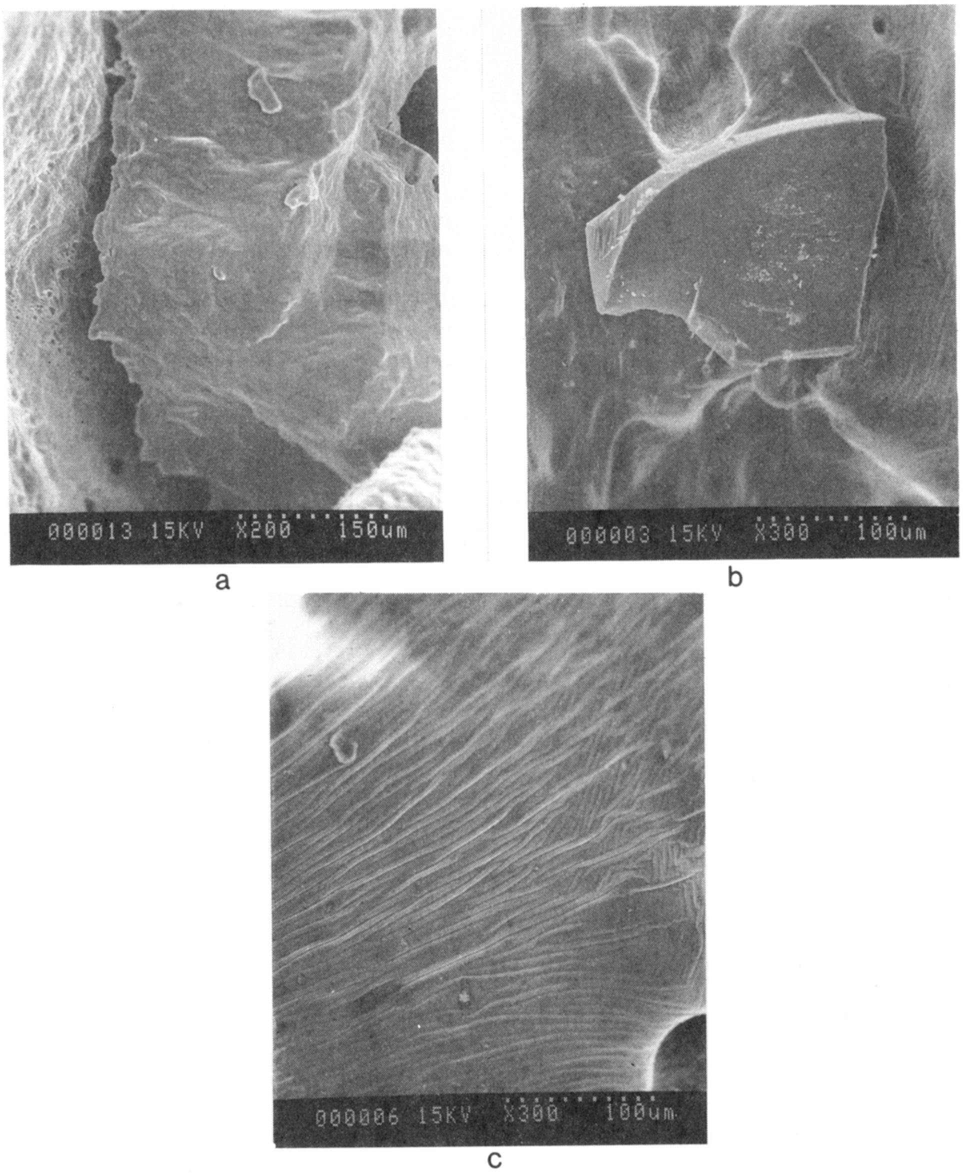


Figure 6. SEM micrographs of PEO(75)/P2VP(25)/$LiClO_4$ complexes: (a) EO/Li = 20; (b) EO/Li = 10; (c) EO/Li = 5.

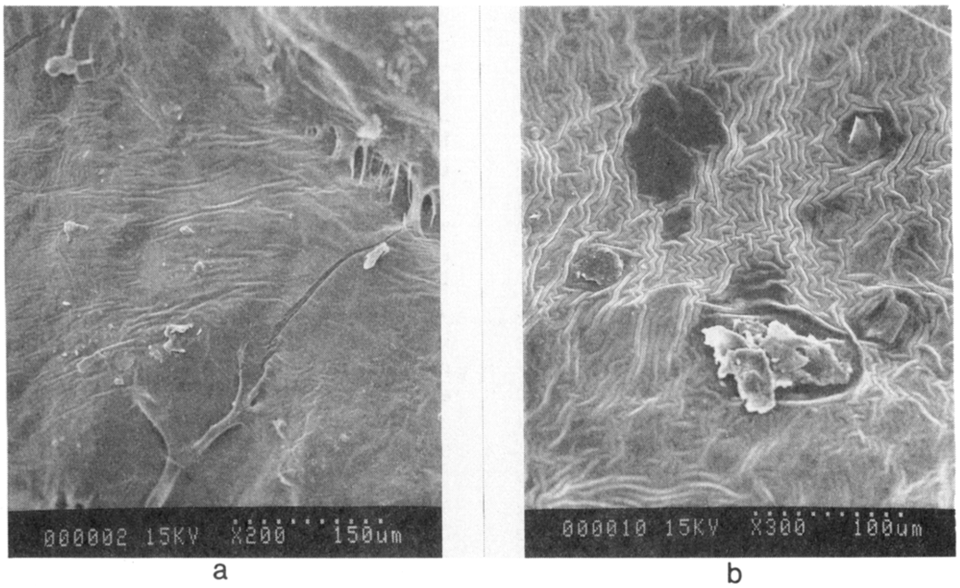
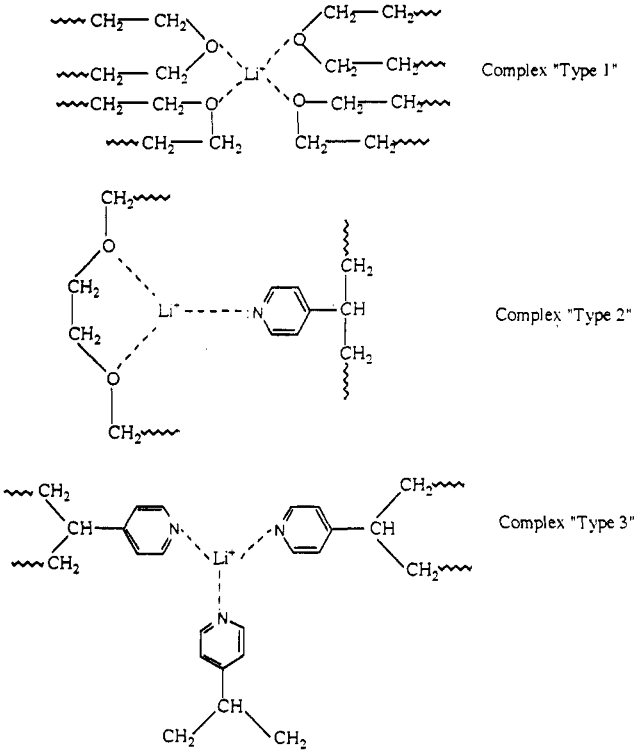


Figure 7. SEM micrographs of PEO(75)/P4VP(25)/$LiClO_4$ complexes: (a) EO/Li = 10; (b) EO/Li = 6.

$LiClO_4$ mole ratios of 50, 35, 25, and 15 are 107, 110, 117, and 130 °C, respectively. This indicates that poly(vinylpyridine) is able to dissolve $LiClO_4$ salt, most likely by a mechanism (i.e. ion–dipole) similar to poly(ethylene oxide). The exact structure of poly(vinylpyridine)/$LiClO_4$ complexes is not known at the present time.

The conductivities and thermal data may be reasonably explained by invoking the presence of three distinct types of ion–dipole complexes as depicted in III.[38] Complexes of "type 1" are present in the pure PEO phase and of "type 3" in the pure P2VP or P4VP phase. Complexes of "type 2" are instrumental in stabilizing the two phase microstructure and are present in the interphase. Further, it is reasonable to assume that ions participating in complexes of types 1 and 2 are mobile and hence contribute to ionic conductivity. Ions in complexes of type 3 are present in a hard phase with little segmental motion at ambient temperature and thus are mostly immobile or do not appreciably contribute to ionic conductivity. The thermal and conductivity behavior of PEO(85)/P2VP(15)/$LiClO_4$ and PEO(75)/P2VP(25)/$LiClO_4$ are compared in Table I. The increase in T_g at the higher salt content of the PEO(85)/P2VP(15)/$LiClO_4$ system is most likely because of the preferential formation of complexes of types 1 and 2. At the higher salt content the pure P2VP phase is probably totally saturated with $LiClO_4$ and formation of complexes of type 3 is not possible. Preferential formation of complexes of types 1 and 2 increase the number of charge carriers, resulting in an increase in ionic conductivity values. However, as more complexes of type 1 are formed, the segmental motion decreases and an increase in T_g is observed.[15] The decrease is segmental motion, as indicated by a T_g increase, reduces the mobilities of the charge carriers, and hence the ionic conductivities decrease. Wintersgill et al. have demonstrated that large scale segmental motion plays an important role in transporting ions in polymer/salt complexes.[39] A T_g increase is not observed with increasing salt content in the range studied for the blend with 25% P2VP content. Also the conductivity increases linearly with salt as the salt concentration is increased. In this case as $LiClO_4$ is added, there is a larger increase in the relative concentration of complexes of types 2 and 3 than complexes of type 1. Complexes of type 2 contribute to ionic conductivity but not an increase in the T_g of the pure PEO/$LiClO_4$ phase. Complexes of type 2 are present in the interphase between the two pure phases and do not affect the thermal behavior of the pure PEO/$LiClO_4$ phase. This suggests that at 25% poly(2-vinylpyridine) content, the higher concentration of the nitrogen atoms allows for the increased formation of complexes of types 2 and 3. Another interesting observation is that while the glass transition temperatures of the PEO(75)/P2VP(25)/$LiClO_4$ blends are lower than those of the PEO(85)/P2VP(15)/$LiClO_4$ blends, the ionic conductivities are also lower. In the area of ionic conductive polymers, lower glass transition temperatures generally translate into higher conductivities. This contrasting behavior is possible because, in the blends with the higher PEO content, there is a larger number of lattice sites through which ion transport is possible. Both a low activation energy of movement of mobile ions and an excess of acceptable lattice sites are required for high ionic conductivity.[40] Ions coordinated solely to the pyridine units (type 3) are present in the hard phase and do not appreciably contribute to ion transport. This is because a high degree of segmental motion in the polymer is the single most important factor governing ionic mobilities.[39] The same reasoning rationalizes the different conductivity and thermal behavior of PEO(85)/P4VP(15)/$LiClO_4$ and PEO(75)/P4VP(25)/$LiClO_4$ blends. Blends containing 35% poly(vinylpyridine) contents exhibit lower conductivities because of the larger volume fraction of the nonconductive P2VP or P4VP/$LiClO_4$ phase. The blends containing 15% and 25% poly(2- or 4-vinylpyridine) are elastomeric materials with excellent dimensional stability. Blends containing 35% P2VP or P4VP are brick hard materials.



III

Conclusion

Our studies demonstrate that a simple methodology like the solution blending of commercial polymers and $LiClO_4$ is a viable technique to prepare inexpensive solid polymer electrolytes with desired properties. By study of a number of different blend compositions, optimum compositions necessary to prepare appropriate materials have been determined. The PEO(85)/P2VP(15)/$LiClO_4$ blend at an ethylene oxide/Li^+ mole ratio of 10 exhibits ionic conductivity values of 1.0×10^{-5} S cm^{-1} at 25 °C and is an elastomeric material with dimensional stability. These properties are suitable for application of the blends as the solid polymer electrolytes in solid state batteries. Furthermore, the blend exhibits ionic conductivities $>3.0 \times 10^{-6}$ S cm^{-1} at 25 °C over a wide salt concentration range (Figure 2). This broad ionic conductivity maximum, as compared to the sharp maxima for most polymer salt complexes,[15,16] provides an additional advantage for application as solid polymer electrolytes. A slight variation in salt concentration, via precipitation or otherwise, will not significantly affect the ionic conductivity and hence power output of a solid state battery. In addition to the PEO(85)/P2VP(15)/$LiClO_4$ blend at an ethylene oxide/Li^+ mole ratio of 10, several other blends have been developed which are also suitable for applications in a variety of microelectronic devices.

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