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King Saud University

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Plasticizing Effect of K⁺ Ions and Succinonitrile on Electrical Conductivity of [Poly(ethylene oxide)−Succinonitrile]/KI−I₂ Redox-Couple Solid Polymer Electrolyte

Ravindra Kumar Gupta[†] and Hee-Woo Rhee*[,‡]

[†]CRC, Department of Optometry College of Applied Medical Sciences, King Saud University, Riyadh 11433, Saudi Arabia
[‡]Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Korea

ABSTRACT: The plasticizing effect of the K⁺ ions and succinonitrile on the electrical conductivity of a new redox-couple solid polymer electrolyte system, $(1 − x)[0.5\text{poly-(ethylene oxide)}:0.5\text{succinonitrile}]:x[0.9\text{KI}:0.1\text{I}_2]$ with $x = 0−0.2$ in weight fraction, is reported. An increase of x resulted in an increase of the electrical conductivity $(\sigma_{25°C})$ of the electrolyte. The electrolyte with $x = 0.15$ exhibited the highest $\sigma_{25°C}$ value, $\sim7 \times 10^{-4}$ S cm⁻¹, and is referred to as the optimum conducting composition (OCC). In addition to an increase of the mobile ion concentration with increasing x, X-ray diffractometry, Fourier-transform infrared spectroscopy, polarized optical microscopy, UV−vis spectroscopy, and differential scanning calorimetry studies revealed a decrease of poly(ethylene oxide) crystallinity/an increase of ionic mobility, indicating the plasticizing effect of the K⁺ ions. Plasticizing and molecular diffusing properties of the succinonitrile further helped to improve the electrical conductivity of the electrolyte.
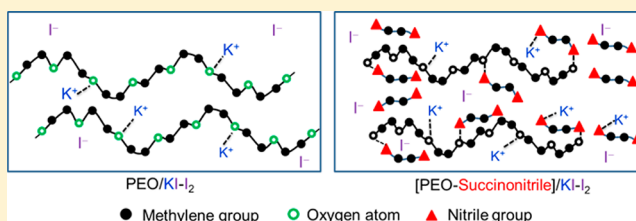
INTRODUCTION

Following the problems of global warming, energy crises, and nuclear hazards, the area of low-cost dye-sensitized solar cells (DSSCs) has been investigated worldwide as an alternative to expensive silicon-based solar cells.[1] At present, a liquid electrolyte-based DSSC exhibits an energy conversion efficiency (η) as high as 11.9% under solar irradiation of 100 mW cm⁻².[2] Use of liquid electrolyte may create problems, such as leakage/evaporation of organic solvent at ambient conditions, electrode corrosion, a need for hermetic sealing, and scale up of the manufacturing process. This shows a requirement for solid polymer electrolytes in order to develop robust, economical, and efficient DSSCs operating at 60−80 °C.[3−5]

High molecular weight poly(ethylene oxide), acronym PEO, is one of the most utilized polymeric matrices of solid polymer electrolytes.[6−8] It offers properties such as self-standing film forming, thermal stability up to 200 °C, eco- and biobenign, relatively low material cost, dissociation/complexation of salt, and segmental motion of polymeric chains for ion transport through ethereal oxygen. PEO/MI−I₂ (M = alkali ion) redox-couple solid electrolytes exhibited $\sigma_{25°C}$ in a range of $10^{-6}−10^{-5}$ S cm⁻¹ due to high PEO crystallinity.[3−5,9−15] Moreover, scanning electron microscopy and atomic force microscopy revealed poor interfacial contact between the electrolyte and dye-sensitized TiO₂ at nanopores due to a large coil size of PEO resulting in η of 0.01−1.8% under solar irradiation of 100 mW cm⁻².[9,12,13,15] Kang et al.[16] observed a limiting value, e.g., $\sigma_{25°C} \geq 10^{-4}$ S cm⁻¹ and PEO molecular weight ≤ 2000 g mol⁻¹ (coil size ≈ 2.82 nm) for the DSSC application.

Use of ether-based plasticizer, e.g., poly(propylene glycol),[9] poly(ethylene glycol),[14,17] poly(ether urethane),[15] and poly-(ethylene glycol) dimethyl ether,[16] largely improved the electrical conductivity of the PEO/MI−I₂ electrolytes via decreasing the PEO crystallinity. It also resulted in significantly improved interfacial contact at nanopores and thus cell efficiency. Several other methodologies, such as blending with poly(vinylidene fluoride),[18,19] plasticization using ionic liquid,[11−14] copolymerization,[4] dispersion of an inorganic nanofiller,[20] and mixing of cations of different ionic radii,[21] worked in a similar fashion and improved cell efficiency. Vittadello et al.[22] showed that alkali iodide can be replaced by an alkaline earth metal iodide (e.g., MgI₂), where species like Mg²⁺, [MgI]⁺, and MgI₂ participate in the conduction process.

Succinonitrile, a plastic crystal between −35 (crystal to plastic crystal phase transition temperature, T_{pc}) and 54 °C (melting temperature, T_m), has had immense widespread interest in recent years.[23−29] It exhibits various interesting features, such as low molecular weight, low T_m value, waxy nature, economically cheap, high molecular diffusivity via trans−gauche isomerization (involving rotation about the central C−C bond) of the molecules and molecular jumps from one diagonal position of the cubic structure to another, high dielectric constant (~55 at 25 °C), and plasticizing property. These features yielded electrolytes with high ionic conductivity ($10^{-4} −10^{-3}$ S cm⁻¹) and high iodine ion diffusivity ($\sim10^{-6}$ cm² s⁻¹) at 25 °C.[28,29] However, the low T_m value (~40 °C) and high-temperature instability of the electrolyte limits its utility for robust DSSCs.

Gupta et al.[30] recently noticed that a blend with an equal weight fraction of high molecular weight PEO and succinonitrile exhibits $\sigma_{25°C}$ two orders of magnitude higher than that of pure PEO. The plasticizing property of succinonitrile effectively reduced the PEO crystallinity. The blend also showed thermal stability better than succinonitrile. One can also expect improved interfacial contact between the dye-sensitized TiO_2 and electrolyte due to the waxy nature and low molecular weight of succinonitrile. These features motivate us to apply the blend as a polymeric host-matrix instead of PEO or succinonitrile for preparing a redox-couple solid electrolyte. We observed better electrical properties for the blend/LiI−I_2 electrolyte relative to the PEO/LiI−I_2 electrolyte.[31]

In the present paper, we report the plasticizing effect of K^+ ions and succinonitrile on the electrical conductivity of a new redox-couple solid polymer electrolyte system, $(1 − x)$-blend:x[0.9KI:0.1I_2] with $0 \leq x \leq 0.2$ in weight fraction. KI was used as an ionic salt because K^+ ion assists in separating the polymeric chains and thus acts as a plasticizer.[10,21,32] We varied the composition (x) for optimizing $\sigma_{25°C}$, and the result was compared with that of the $(1 − x)$PEO:x[0.9KI:0.1I_2] system. The $\sigma_{25°C} − x$ variation was explained using structural, optical, and thermal studies.

■ EXPERIMENTAL SECTION

Commercially available Sigma-Aldrich chemicals with purity greater than 99% were used for preparing solid electrolytes without further purification. The molecular weight of the PEO was 1 M g mol^{-1}. A homogeneous solution was obtained through dissolving the precursors in anhydrous acetonitrile (99.8%, Aldrich) and continuously stirring it at 60 °C for 24 h. Casting of the solution on a Teflon Petri dish followed by drying in nitrogen gas atmosphere at room temperature for a couple of weeks and further drying under vacuum at 28 °C for a day led to a thick film. The self-standing thick films of the electrolytes were achievable up to $x = 0.15$ only, though salt was dissolvable up to $x = 0.2$. Therefore, electrical conductivity measurement was performed for the blend/KI−I_2 electrolytes with $x = 0−0.15$ only. The PEO/KI−I_2 electrolyte system with $x = 0−0.25$ in weight fraction was also prepared in a similar manner for the σ study.

Samples were characterized using a Solartron impedance analyzer (model 1252A) coupled with an SI 1287 electrochemical interface, a Rigaku X-ray diffractometer (XRD, model D-MAX 2500), a Thermo Electron Fourier-transform infrared spectrometer (FT-IR, model Nicolet 380), a Nikon polarized optical microscope (model Optiphot-2 Pol), a Jasco UV−visible spectrophotometer (model V550), and a TA Instruments differential scanning calorimeter (DSC, model MDSC 2910). Details of characterization techniques are described elsewhere.[30,31]

■ RESULTS AND DISCUSSION

Electrical Property. Figure 1 shows $\sigma_{25°C} − x$ variation of the solid electrolyte systems: $(1 − x)$blend:x[0.9KI:0.1I_2] and $(1 − x)$PEO:x[0.9KI:0.1I_2]. The figure also shows the EO/[K^+] mole ratio in parentheses. The PEO/KI−I_2 electrolyte system exhibited an increase of $\sigma_{25°C}$ value with increasing x up to $x = 0.25$ (optimum $\sigma_{25°C}$ value, ~2 × 10^{-5} S cm^{-1}; EO/[K^+] ≈ 12.6) followed by a decrease for $x = 0.3$. The trend is similar to the $\sigma_{25°C} − x$ curve reported by other groups.[10,11] It is also similar to that of the $(1 − x)$PEO:xKI electrolyte system
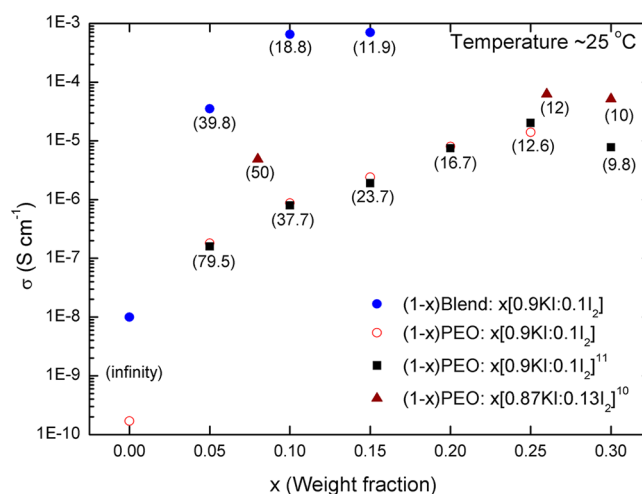
Figure 1. $\sigma−x$ curves of the $(1 − x)$blend:x[0.9KI:0.1I_2] and $(1 − x)$PEO:x[0.9KI:0.1I_2] solid polymer electrolyte systems including those reported by other groups.[10,11] Data in parentheses correspond to EO/[K^+] mole ratio.

without I_2.[32] The blend/KI−I_2 electrolyte system also exhibited an increase of $\sigma_{25°C}$ value with increasing x up to $x = 0.15$ (optimum conducting composition, OCC; $\sigma_{25°C} \approx 7 × 10^{-4}$ S cm^{-1}; EO/[K^+] ≈ 12). It is two orders of magnitude higher than the σ value, ~2 × 10^{-6} S cm^{-1} of the 0.85PEO:0.15-[0.9KI:0.1I_2] electrolyte prepared identically with a similar weight fraction, i.e., $x = 0.15$ without succinonitrile for direct comparison. It is also worth mentioning that the $\sigma_{25°C}$ value for the blend/KI−I_2 electrolyte is higher than that of the blend/LiI−I_2 electrolyte.[31]

The trend of $\sigma_{25°C} − x$ curve, i.e., an increase of σ up to an optimum value with increasing x followed by a decrease, is a commonly observed phenomenon in solid polymer electrolyte systems and composite electrolyte systems.[6−8,33,34] According to a general expression of electrical conductivity, $\sigma = nq\mu$, one can assert that an increase in σ is due to either an increase in mobile ion concentration (n) or ionic mobility (μ) or both, where q is a constant (the charge on the mobile ion). In the PEO/KI−I_2 solid electrolyte system, PEO helped to dissociate ionic salt, resulting in an increase in n with increasing x.[10,11,32−34] It also helped in K^+ ion transport through its ethereal group. K^+ ions also acted as plasticizer to separate out polymeric chains through interaction between K^+ ion and ethereal oxygen of the PEO. In addition, owing to segmental motion of neighboring polymeric chains, one can also expect an increase in μ with increasing x.[10,11,32−34] For electrolytes with $x \geq 0.3$, Coulombic interaction between ions starts to dominate, resulting in formation of ionic pairs, ionic multiplets, and/or salt aggregation, and thus a decrease of n.[6−8,10,33,34] It may also be associated with a decrease of μ via immobilization of polymeric chains due to formation of cross-linking O−K^+−O between oxygen atoms of different polymeric chains.

The blend/KI−I_2 electrolyte exhibited electrical properties superior to that of the PEO/KI−I_2 electrolyte. It is most probably due to a large decrease of PEO crystallinity by plasticizing property and trans−gauche isomerism of succinonitrile as observed below.[24−27,31] A decrease of PEO crystallinity enhances the rate of transition from gauche to trans and thus increases the trans conformer concentration. The trans isomer acts as an impurity, resulting in enhancement of lattice defects and lowering of activation energy for ionic conduction. In

addition, owing to an interaction between ethereal oxygen of PEO and nitrogen of succinonitrile as discussed below, there is a high probability for competition between ethereal oxygen and nitrogen to bind K^+ ions, resulting in more free ions for conduction.[24−27]

Structural Properties. Figure 2 shows the XRD pattern of the solid electrolyte systems: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with
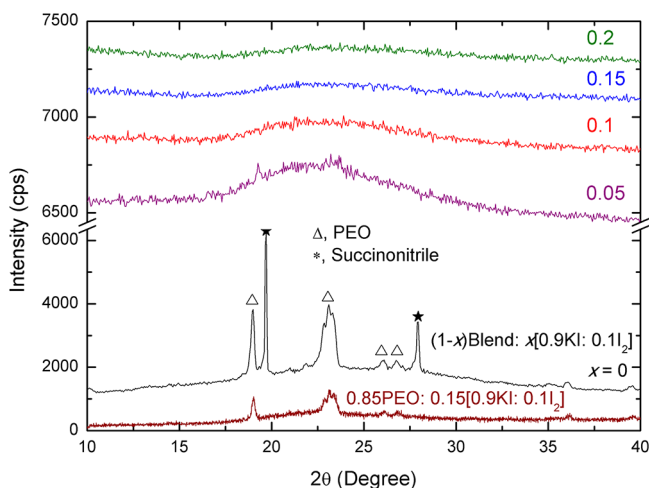
Figure 2. X-ray diffractograms of the solid polymer electrolyte systems: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0–0.2$ in weight fraction and $0.85PEO:0.15[0.9KI:0.1I_2]$.

$x = 0–0.2$ and $0.85PEO:0.15[0.9KI:0.1I_2]$. The diffractogram of the blend $(x = 0)$ comprised of the reflection peaks of the PEO and succinonitrile indicate its composite nature.[7,30] The absence of reflection peaks of KI and I_2 in the diffractograms of the electrolytes $(x = 0.05–0.2)$ indicated a perfect salt complexation with the polymeric matrix.[10,32] Reflection peaks of KI were noted in the X-ray diffractogram of the electrolyte with $x = 0.25$ (data not shown). It is due to the lower Gutmann donor number of the nitrile of the succinonitrile with respect to the ethereal oxygen of the PEO for solvating cations.[23] For a small fraction of salt concentration $(x = 0.05)$, the electrolyte observed a significant reduction of the reflection peaks of the PEO and succinonitrile, while no reflection peaks were noticed for electrolytes with $x = 0.1–0.2$. A similar trend, i.e., a decrease of PEO reflection peak intensity with increasing x, was noted for the PEO/KI system with and without I_2.[10,32] For $x = 0.15$ the intensity of PEO's reflection peaks was low, while no peaks were noted for $x = 0.25$. This infers that an increase of x led to K^+ ions complexation with the ethereal oxygen of PEO, resulting in a reduction in PEO crystallinity.[6−8,10,32] Owing to the plasticizing property of the succinonitrile and a competition between the ethereal oxygen and the nitrogen to coordinate K^+ ions, one can expect a large decrease of PEO crystallinity as well as a large increase of free K^+ concentration.[25−27] The plasticizing property of the K^+ ions and succinonitrile is also visible by the FT-IR spectroscopy study, which is discussed below.

Figure 3 shows FT-IR spectra of the $(1 − x)$-blend:$x[0.9KI:0.1I_2]$ with $x = 0–0.2$. The FT-IR spectrum of the blend $(x = 0)$ comprises spectra of PEO and succinonitrile, indicating its biphasic nature.[30] Table 1 lists the observed vibrational frequencies of the blend $(x = 0)$ along with those of the constituents, pure PEO[31,35] and succinonitrile.[31,36] It showed an interaction of the ethereal oxygen of PEO with
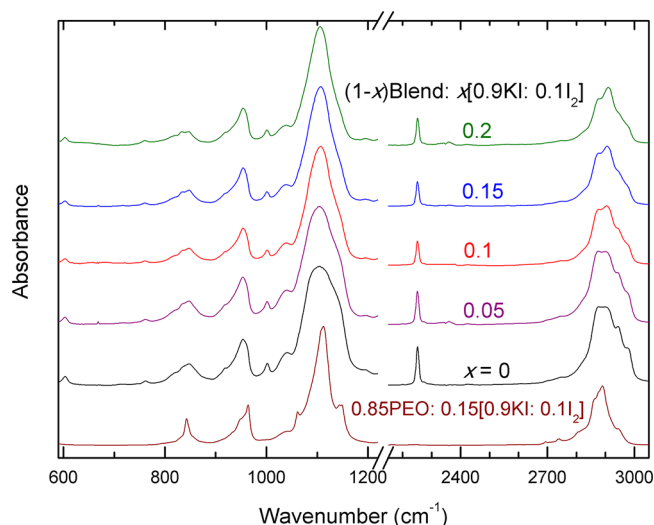
Figure 3. FT-IR spectra of solid polymer electrolyte systems: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0–0.2$ in weight fraction and $0.85PEO:0.15[0.9KI:0.1I_2]$.

nitrogen of succinonitrile via shifting of the PEO's $\nu_{a,COC}$ band from 1109 to 1104 cm^{-1} and succinonitrile's $\nu_{C≡N}$ band from 2254 to 2251 cm^{-1}. One can observe a significant modification in the PEO chain conformation via a shifting in the CH_2-based band's position (relative to those of pure PEO): $\rho_{a,CH2}$ at 953 (963 cm^{-1}), $t_{a,CH2}$ at 1251 (1242 cm^{-1}), $\omega_{a,CH2}$ at 1350 (1342 cm^{-1}), and $\nu_{a,CH2}$ at 2899 (2889 cm^{-1}). It is also substantiated by the appearance of two new weak bands at 1040 and 1299 cm^{-1} and merging of shoulder $\nu_{a,COC}$ bands to the central $\nu_{a,COC}$ band at 1104 cm^{-1}. It suggests entangling of PEO chains in the succinonitrile domain with a contracted C−H bond and twisted chains, which helped to decrease the PEO crystallinity. This indicates that succinonitrile is a good plasticizer for the PEO. It also worth mentioning that succinonitrile possesses vibrational modes of gauche and trans isomers.[31,36]

FT-IR spectra of $(1 − x)$blend:$x[0.9KI:0.1I_2]$ electrolytes with $x = 0.05–0.2$ are similar to those of the blend $(x = 0)$ and blend/LiI−I_2 electrolyte,[31] whereas the FT-IR spectrum of the $0.85PEO:0.15[0.9KI:0.1I_2]$ electrolyte, included in the Figure 3, is similar to that of the pure PEO.[30,31] Therefore, the observed frequencies for the electrolytes are assigned accordingly and shown in Table 1 for direct comparison. The effect of x is visible by an upshift of the PEO's $\nu_{a,COC}$ band from 1104 ($x = 0$; blend) to 1107 cm^{-1} ($x = 0.15$) for the blend/KI−I_2 electrolyte and 1109 ($x = 0$; PEO) to 1113 cm^{-1} ($x = 0.15$) for the PEO/KI−I_2 electrolyte. It is due to salt complexation phenomenon, indicating interaction of ethereal oxygen with K^+ ions for ion transport.[22,31] It is worth mentioning that the blend/KI−I_2 electrolyte portrayed less upshift relative to the PEO/KI−I_2 electrolyte for $x = 0.15$. It is most probably due to the succinonitrile that is also competing to coordinate K^+ ion through its nitrogen.[25,26] The blend/KI−I_2 electrolyte also showed a broadening of peaks in a region of 800−890 cm^{-1} with increasing x. The plasticizing effect of succinonitrile is visible at the PEO's $\nu_{a,CH2}$ band, which was up shifted from 2899 ($x = 0$; blend) to 2906 cm^{-1} ($x = 0.15$), indicating C−H bond contraction,[30,31] while no significant upshift in the $\nu_{a,CH2}$ band was observed for the $0.85PEO:0.15[0.9KI:0.1I_2]$ electrolyte. Vital roles of K^+ ions and succinonitrile in reducing the PEO crystallinity are quite observable below by the polarized optical microscopy and UV−vis spectroscopy studies.

Table 1. Observed Vibrational Frequencies (in cm^{-1}) of the PEO/KI−I$_2$ and Blend/KI−I$_2$ Solid Polymer Electrolytes with x = 0.15^a

PEO^{b,c}	PEO/KI−I$_2$^{c}	succinonitrile^{c,d}	blend^c	blend/KI−I$_2$^{c}	assignment^e
		604{604}s	604m	604m	δ_{CCC} (B)
		762{762}s	762m	762m	δ_{CH2} (A$_u$)
		819{820}s	819vw	819vw	ν_{C-CN} (A)
843{844}s	843m		846m	847m	$\rho_{a,CH2}$ (E$_1$), ν_{CO} (E$_1$)
		918{918}s	918sh	918sh	ν_{C-CN} (B$_u$)
963{958}s	963s	963{963}vs	953s	954s	$\rho_{a,CH2}$ (A$_2$); ν_{C-CN} (B)
		1002{1002}vs	1002m	1001m	ρ_{CH2} (A)
1061{1060}m	1061sh		sh	sh	$\nu_{a,COC}$, $\rho_{a,CH2}$ (E$_1$)
1109{1103}vs	1113vs		1105vs	1107vs	$\nu_{a,COC}$ (A$_2$)
1149{1147}s	1144sh		sh	sh	ν_{CC}, $\nu_{a,COC}$ (E$_1$)
		1199{1198}m	1196vw	1195vw	t_{CH2} (B)
		1233{1232}s	sh	sh	t_{CH2} (A)
1242{1240}m	1242m		1251m	1251m	$t_{a,CH2}$ (A$_2$)
		1272{1272}m			ω_{CH2} (B$_u$)
1280{1278}m	1280m		1299m	1299m	$t_{a,CH2}$, $t_{s,CH2}$ (E$_1$)
		1337{1337}s	sh	sh	ω_{CH2} (B)
1342{1342}s	1343s		1350m	1352m	$\omega_{a,CH2}$ (A$_2$)
1359{1358}m	1360sh				$\omega_{s,CH2}$, ν_{CC} (E$_1$)
		1426{1426}vs	1426s	1424s	δ_{CH2} (A)
1454{1454}m	1454m		1453w	1454w	$\delta_{a,CH2}$ (A$_2$)
1467{1466}m	1467m		1469w	1470w	$\delta_{a,CH2}$, $\delta_{s,CH2}$ (E$_1$)
		2254{2254}vs	2251s	2252s	$\nu_{C\equiv N}$ (B, B$_u$, A)
2861{2859}sh	2861sh		2875s	2878sh	$\nu_{s,CH2}$ (A$_2$)
2889{2888}vs	2890vs		2899s	2906vs	$\nu_{a,CH2}$ (A$_2$)
		2952{2951}s	2943sh	sh	$\nu_{s,CH2}$ (B, B$_u$, A)
		2989{2989}s	2975sh	sh	$\nu_{a,CH2}$ (B, A$_u$, A)

^{a}Vibrational frequencies of PEO, succinonitrile, and blend are also included. ^{b}Vibrational frequencies of the PEO, denoted in curly brackets, are reported by Yoshihara et al.[35] ^{c}Relative intensity is marked by vw (very weak), w (weak), m (medium), s (strong), vs (very strong), and sh (shoulder). ^{d}Vibrational frequencies of the succinonitrile (trans and gauche), denoted in curly brackets, are reported by Fengler and Ruoff.[36] ^{e}Assignment corresponds to stretching (ν), bending (δ), wagging (ω), twisting (t), and rocking (ρ) modes. Suffixes s and a denote the symmetric and asymmetric vibrational modes, respectively.
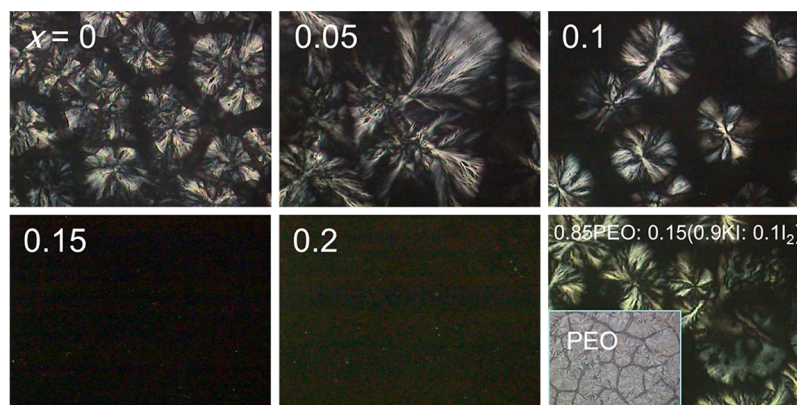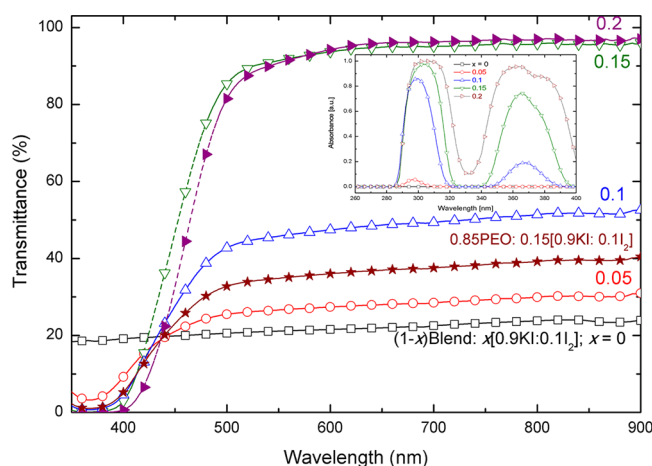

Figure 4. Polarized optical micrographs (POMs) of solid polymer electrolyte systems: $(1 − x)$blend:x[0.9KI:0.1I$_2$] with x = 0−0.2 in weight fraction and 0.85PEO:0.15[0.9KI:0.1I$_2$]. (Inset) POM of pure PEO. Magnification, 400×.

Optical Properties. Figure 4 shows polarized optical micrographs (POMs) of the $(1 − x)$blend:x[0.9KI:0.1I$_2$] with x = 0−0.2. POMs of the pure PEO and 0.85PEO:0.15-[0.9KI:0.1I$_2$] electrolyte are also shown for direct comparison. The image of blend (x = 0) portrayed a large number of PEO spherulites in the dark region. The dark region corresponds to a highly conductive amorphous area.[27,30,32] At low salt concentration (x = 0.05), PEO lamellae are weakly and randomly oriented. At x = 0.1, salt complexation resulted in only a few PEO spherulites with largely reduced size and extended dark region. The plasticizing effect of K$^+$ ions is prominent for x = 0.15 and 0.2, which resulted in completely weak and randomly oriented PEO chains as indicated by a complete dark region. The $(1 − x)$PEO:xKI electrolyte system also portrayed a similar trend, i.e., a decrease of the number and size of PEO spherulites and extension of the dark region with increasing x.[32] However, attaining a complete dark region for the 0.85blend:15[0.9KI:0.1I$_2$] electrolyte relative to that of 0.85PEO:15[0.9KI:0.1I$_2$] electrolyte infers that the plasticizing property of succinonitrile is useful to obtain completely weak

and randomly oriented PEO chains. This observation is corroborative to the UV−vis spectroscopy study discussed below.

Figure 5 shows UV−vis transmittance spectra of the $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0−0.2$ and 0.85PEO:0.15-

Figure 5. UV−vis spectra of solid polymer electrolyte systems: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0−0.2$ in weight fraction and 0.85PEO:0.15$[0.9KI:0.1I_2]$. (Inset) Absorption spectra of the $(1 − x)$blend:$x[0.9KI:0.1I_2]$ in a region of 260−400 nm.

$[0.9KI:0.1I_2]$. The blend $(x = 0)$ exhibited transmittance of nearly 20% in the entire UV and visible regions probably due to the availability of a large number of PEO spherulites. Salt complexation led to the electrolytes being opaque in the UV region due to the I^-/I_3^- redox couple.[1] As shown in the inset of the figure, absorption spectra of electrolytes exhibited peaks at 298 nm for $x = 0.05$, 300, and 368 nm for $x = 0.1$, 304, and 366 nm for $x = 0.15$, 306, and 364 nm for $x = 0.2$ with increasing intensity. It is due to I_3^- radicals, whose concentration increased with increasing x.[19] Electrolyte with $x = 0.2$ may also have higher polyiodide ions, e.g., I_5^- as obvious by broad and multiple peaks.[10] In the visible and near-infrared regions with a wavelength range of 500−900 nm, transmittance increased with increasing x. The blend/KI−I_2 electrolytes with $x = 0.15−0.2$ possessed optimum transmittance of nearly 94%. We noted the transmittance spectrum of the 0.85PEO:0.15$[0.9KI:0.1I_2]$ electrolyte similar to those of the blend/KI−I_2 electrolytes. However, transmittance was nearly 40% only. It indicated that succinonitrile played a vital role in reducing the number and size of PEO spherulites, extending the amorphous region and thus improving the transmittance. A large transmittance of the blend-based electrolyte opens up its utilization for tandem solar cells.[37]

Thermal Property. Figure 6 shows DSC curves for the solid electrolyte systems: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0 − 0.2$ and 0.85PEO:0.15$[0.9KI:0.1I_2]$. DSC curves portrayed endothermic peaks due to the melting temperature (T_m) and glass transition temperature (T_g) of the electrolyte systems. The values of T_m and T_g for the blend and pure PEO-based electrolytes are summarized in Table 2. The blend $(x = 0)$ exhibited an intense T_m peak at 30 °C. A relatively low intensity T_m peak was noticed at 29 °C for the electrolyte with $x = 0.05$. A further increase in x resulted in a largely reduced T_m value and its peak intensity. As shown in the Table 2, PEO/KI−I_2 electrolyte system exhibited a similar trend, i.e., a decrease of T_m value and its peak intensity with increasing x up to its
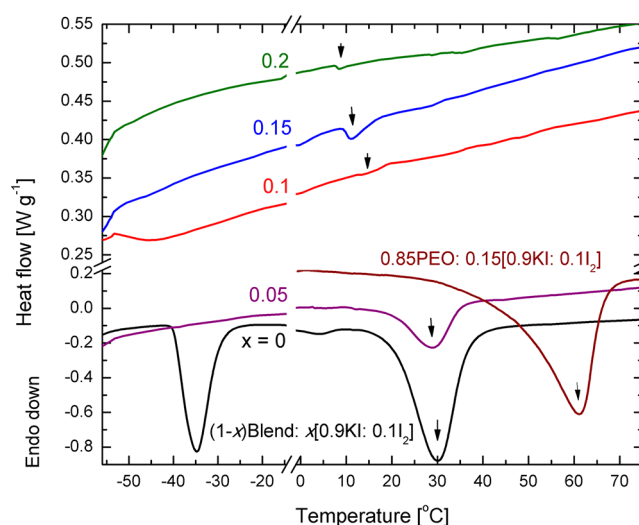
Figure 6. DSC curves of solid polymer electrolyte system: $(1 − x)$blend:$x[0.9KI:0.1I_2]$ with $x = 0−0.2$ in weight fraction and 0.85PEO:0.15$[0.9KI:0.1I_2]$.

Table 2. Melting Temperature (T_m), Relative Crystallinity (χ), and Glass Transition Temperature (T_g) of the Blend and Pure PEO-Based Polymer Electrolytes with Composition x

x [wt fraction]	T_m [°C]	χ [%]	T_g [°C]
$(1 − x)$blend:$x[0.9KI:0.1I_2]$			
0	30.1	25.2	−60
0.05	29.1	8.4	−46.4
0.1	14.6	0	−44.8
0.15	11.5	0.2	−46.1
0.2	8.4	0	−48.1
$(1 − x)$PEO:$x[0.9KI:0.1I_2]$			
0.15	61.1	36.8	
$(1 − x)$PEO:$x[0.87KI:0.13I_2]$[10]			
0	77.2	86.7	−55.46
0.08	72.4	37.6	−40.26
0.26	65.3	7.2	−33.11
0.30	53.4	8.1	−33.75

optimum value. We observed $T_m \approx 61.1$ °C with a reduced intensity for the 0.85PEO:0.15$[0.9KI:0.1I_2]$ electrolyte relative to pure PEO[30] ($T_m \approx 65.7$ °C). It infers that an increase in x decreased the PEO crystallinity. The relative PEO crystallinity (χ) can be quantified by the ratio of change in enthalpy (ΔH_m) of sample to that of the fully crystalline PEO ($\sim$193 J g^{-1}).[30] The χ value of the blend and pure PEO-based electrolyte systems, shown in Table 2, decreased with increasing x. indicating the plasticizing effect of K$^+$ ions. Table 2 also reveals the fact that the blend/KI−I_2 electrolyte possesses a very low χ value with respect to the PEO/KI−I_2 electrolyte for the same x value due to the plasticizing effect of the succinonitrile.

Table 2 also shows that salt complexation resulted in an increase in the glass transition temperature (T_g) of the polymeric matrices, blend, and PEO. It is due to the transient cross-linking between K$^+$ ion and ethereal oxygen, which reduces the number of cross-linking centers of the PEO.[6] However, the plasticizing property of succinonitrile led to a T_g value of the blend/KI−I_2 electrolyte that is lower than that of the PEO/KI−I_2 electrolyte. The effect of trans−gauche isomerism of the succinonitrile on the electrical conductivity of the blend/KI−I_2 electrolyte is apparent at the plastic crystal

phase transition temperature (T_{cp}).[24−27] The blend exhibited an intense T_{cp} peak at −35 °C. It totally disappeared after salt complexation. In general, the presence of impurity, e.g., PEO and K⁺, reduces the trans−gauche energy barrier of the succinonitrile. As mentioned earlier, it leads to an enhanced trans concentration and existence of trans phase at temperatures lower than the T_{cp} of the succinonitrile. Consequently, it helps to increase the ion conduction.

CONCLUSIONS

A new fast ion conducting redox-couple solid polymer electrolyte system, $(1 − x)$ blend:$x[0.9KI:0.1I_2]$, where $0 \leq x \leq 0.2$ in weight fraction, was synthesized. An increase of x helped to increase the electrical conductivity. It was attributed to an increase in mobile ion concentration via salt dissociation by the PEO as well as an increase in ionic mobility due to the plasticizing property of K⁺ ions reducing the PEO crystallinity. The plasticizing property and high molecular diffusivity of the succinonitrile also played a crucial role to improve the electrical conductivity. It resulted in a better interfacial contact between the electrolyte and dye-sensitized TiO_2 at the nanopores and finally an improvement of the photovoltaic property relative to those prepared using the pure PEO-based electrolyte.[38]

AUTHOR INFORMATION

Corresponding Author

*Phone: +82 2 705 8483. Fax: +82 2 711 0439. E-mail: hwrhee@sogang.ac.kr.

Notes

The authors declare no competing financial interest.

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