



Article

Two Promising Methodologies for Dealing with Changes in Optical and Electrical Properties of Polymer Electrolytes (SPEs)

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Abstract: Variation of light absorption, mainly the shift and shape of the absorption edge, are two promising approaches aimed at understanding the fundamental processes of optical transitions in crystalline and amorphous materials. This allows us to better understand the structure of energy bands. Significant advances have been made in understanding the fundamental chemical and physical properties of polymers to improve the efficiency of photovoltaic and optoelectronic devices. However, the relationship between these two properties has not been determined. Characterization of the optical properties of polymers, such as infrared dichroism, light absorption, Raman polarization, and emission spectra, is an important method for studying electronic properties. To consider conductivity and thermal savings in the range (300–500 K), we also investigate the effect of temperature on conductivity. Activation energies found in different cases were used. Ionic conductivity has been found to be temperature-dependent for all SPE formulations. It has been found that the ionic conductivity of the membrane presents two regimes, the first being at relatively low temperatures. The ionic conductivity exhibits a relatively independent behavior of temperature. It was found that the dielectric constant of the SPE polymer electrolytic system increased with increasing temperature. This behavior is typical of pole insulators because the alignment of the dipoles becomes easier with increasing temperature and thus the dielectric constant increases.

Keywords: optical and electrical properties; polymer electrolytes (SPEs); nanocomposite; AC conductivity composite electrolytes



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1. Introduction

Polymeric electrolytes (PEs) were first reported by Fenton et al. They became commercially available in 1973 [1], and their technical importance in large-scale applications occurred in the early 1980s [2]. During the last 30 years, great attention has been paid to the development of new PEs due to their wide applications in electrochemical supercapacitors, storage, and conversion systems [3–7]. Polyelectrolytes (PE) are membranes that contain salts dissolved in a polymeric matrix (of high molecular weight) [8]. Most solids without these solvent systems have ion-conducting properties. Therefore, they have been widely used in many electrochemical devices, such as rechargeable batteries, solid-state batteries, and especially lithium-ion batteries. In recent years, PEs have been widely used in electrical and electrochemical devices, especially electronic and electrochromic devices, rechargeable batteries, Electrical Double Layer Capacitors (EDLC), fuel cells, analog memory devices, and dye-sensitized solar cells (DSSC), and for electrochromic windows and electrochemical sensors [3–7]. Previous studies have shown that various polymer electrolytes with high DC conductivity and an amorphous structure are good materials for rechargeable battery applications due to their low inertia and non-leakage characteristics [9,10]. Based on recent advances, polymer electrolytes are considered new safe candidates for important electrochemical device applications to replace lithium-ion batteries [10–12]. Recent studies have shown that PE is crucial for DSSC applications. O'Regan and Gratzel developed a new

type of solar cell called the DSSC dye solar cell in 1991, whose unique properties made it a new renewable energy source [13]. The electrolyte in DSSC plays an important role as it is responsible for charge transport between the electrodes [14]. In general, electrolytes are divided into different types such as liquid electrolytes, semi-solid electrolytes, and solid electrolytes. Electrolytes have been the subject of extensive research due to their significant impact on the efficiency of solar cells [13–19]. Dry polymer electrolytes are often referred to as solventless electrolytes. It was also shown that positively charged (cations) and negatively charged (anions) ions bind more loosely and are therefore able to migrate. In general, polyethylene oxide (PEO) can be used as a relatively high-molecular-weight solvent-free polymer electrolyte [20]. Unfortunately, the relatively high crystallinity of PEO-based electrolytes at room temperature indicates poor ionic conductivity [20]. Various approaches have been implemented to reduce crystallinity and increase the ionic conductivity of polymer electrolytes, such as salt insertion copolymerization, plasticization, blending, blending with other polymers, addition of fillers/additives, etc. [21]. To be applicable, polymeric electrolytes must possess several properties, especially sufficient ionic conductivity and low electronic conductivity in the range of 10^{-4} to 10^{-5} S cm⁻¹ [21]. In addition, high mechanical and electrochemical resistance with reasonable optical properties (long-term resistance to UV radiation, inconsistent translucency or transparency) is required [22]. It should be noted that the host polymer must have several key properties, such as an efficient electron donor that forms coordinate bonds with cations with little steric hindrance to link polarity and rotation.

Polymeric electrolytes have several advantages over conventional liquid electrolytes. They are phase-based, transparent, solvent-free, flexible and adjustable ionic conductivity, high electrochemical stability, strong film-forming ability, easy processing, high ionic conductivity and light weight. The ion-conducting properties of these electrolytes facilitate the transport of ionic species compared to some ionic liquid electrolytes [23]. The safety of PE is also impressive, suppressing various problems such as internal short circuits, electrolyte leakage, corrosivity, noxious gases, and non-flammable reaction products on the electrode surface [23,24]. Furthermore, macromolecular hosts require certain fundamental properties. For example, they must be a polar polymer with a low barrier to bond rotation and a high electron donating capacity capable of coordination with cations.

Recently, considerable attention has been paid to study the properties of the solid polymer electrolytes (SPEs), due to their technological importance in energy-storage devices such as batteries, supercapacitors, fuel cells, and hybrid power sources [25]. This scientific attention has been focused on a wide range of existing materials, but especially to polymer nanocomposite-based materials, due to their advantages of excellent flexibility and processability, offering a flexible design and the possibility of miniaturization for device fabrication in contrast to liquid materials [25]. To date, the most widely used and investigated dopant nanoparticles are TiO₂, Al₂O₃, SiO₂, and MgO. It was found that adding the nanoparticles to SPEs increases their ionic conductivity and mechanical strength [26].

However, some research focuses on natural polymers such as chitin and chitosan (CS), which are natural amino polysaccharides. These types of polymers have been widely used in various medical applications and biological applications, because of their unique properties [27]. Chitosan, which is derived from chitin, has attracted significant attention as a functional, nontoxic, biodegradable biopolymer for diverse applications. From a chemical point of view, it is heteropolymer, containing both amine (NH₂) and hydroxyl (OH) groups on its backbone [28]. These functional groups explain why CS can undergo complexation with inorganic salts. The results of the ionic conductivity of polymeric materials caused chemists and engineers to accelerate the study of its most important applications, which are in electrochemical devices [29].

As a result, some basic information about the band structure and energy band gap of polymeric materials have been obtained by analyzing the optical absorption spectra. It was found that the visual characterization of polymer composites is useful in determining

the role of defects and in selecting polymeric materials to be used in more common and specific applications [30].

Moreover, it has been shown that hindering the reduction of silver ions by alumina nanoparticles led to an increase in the ionic conductivity of DC. Moreover, the relationship between DC conductivity and dielectric constant revealed the need for further research to understand the basics of ionic conduction in these disordered solids in absorption mode, to record UV-Vis spectra of the three-layer membrane of chitosan, silver, and nanocomposites, which has motivated authors to work on such important topics [31].

Previous studies showed that the first synthetic polymer used as a polymer electrolyte solution was polyethylene oxide (PEO). PEO is a linear semi-crystalline polymer that has a lot of features, such as being non-toxic, thermally stable, flexible, hydrophobic and cost-effective [32]. Despite all these advantages of PEO, it has poor ionic conductivity due to its high degree of crystallinity, and therefore, it is impossible for it to achieve high DC conductivity; it is this factor that has made modulators study the polymer with new methods to reach different results. The poor ionic conductivity of PEO can be improved by adding or increasing a plasticizer, acid, salt, or other conductive polymer [33].

However, it is known that PEO is the most suitable polymeric material for electrolytes based on solid polymers, and some research shows that by preparing a polymer mixture of PEO/PVP, the optical band gap is strongly affected by the incorporation of silver nanoparticles [34]. In this context, sodium carboxymethyl cellulose (CMC) has been chosen to form a mixture with PEO to increase the amorphous fractions within PEO because CMC is a semi-crystalline polymer. Since these two polymers have a common solvent (water), a strong interaction between CMC and PEO occurs via the (-O-) ether group of PEO and both the carboxylic and hydroxyl groups of CMC, which is a naturally occurring, organic, non-toxic polysaccharide polymer. Moreover, CMC is involved in many industrial applications such as foodstuffs, paper, paints, cosmetics, and pharmaceuticals. Therefore, most of the research aims to present a new solid polymer electrolyte based on plasticized CMC/PEO mixtures. By controlling the crystalline regions of PEO and the amorphous regions of CMC, new combinations of CMC/PEO suitable for photovoltaic and photonic devices can be obtained [34].

In order to reach the best form of electron transmission, there has been much research in which the study of optical insulator loss has been applied. SPEs usually consist of a host polymer matrix that acts as a transport pathway for conductive ions and a specific fraction of salts that produce conductive ions [35,36]. Over the past years, various types of ion-conducting SPEs with a wide range of polymer matrices, such as PMMA, NaAlg, PEO, PVP, PVdF, and PVA, have been extensively investigated for a host polymer electrolyte. Among them, PVA has been shown as a potential host polymer electrolyte due to its semi-crystalline structure, biocompatibility, high chemical stability, high film-forming efficiency, high value for dielectric toughness, good film-fabrication ability, and dopant-dependent conductive properties. Additionally, for all these properties, the demand for such types of polymers has become very large.

Therefore, we were motivated to study the optical and electrical properties of the nanocomposite solid polymer and the possibility of benefiting from it in optical and electrical applications. It was found that the incorporation of nanoparticles reduced the bandgap of the nanocomposite.

2. Experimental Work

Polymer Salt Complex and Dry Solid Polymer Electrolytes (SPEs)

Dried SPEs were prepared by dissolving ionic inorganic salts in a coordinated polar polymer. The desired dry SPE was mainly prepared using high-molecular-weight polymers, polyethylene oxide (PEO) and polypropylene oxide (PPO), conjugated with various lithium ion salts. Various lithium salts were used for complexation with PEO to produce the SPE LiX membrane (where X = 1 [pure], Br, CF₃SO₃, BF₄, AsF₆) [37]. The dry PEO solid polymer electrolyte interacted with the Li⁺ salt, as shown in Figure 1. -CH₂-CH₂-O- and the pres-

ence of polar groups was observed. The chains of polymeric compounds -O-, -H-, -C-H-, PEO/PPO increase their solvency and subsequently form complexes of ionic salts [35,37]. The elongation of polymer-salt complexes depends on the competition between the lattice energies of the polymer and the inorganic salt, as well as on solvation [38]. Here, this focus on the optical properties of polymers is explained in terms of their widespread use in optical devices [39,40]. The purpose of tuning the optical properties in this study was to achieve optimal reflection, anti-reflection, interference, and polarization properties [39]. We successfully achieved the modification of optical properties through the doping incorporation process [39]. The incorporation of such dopants into a polymer matrix resulted in a change in the chemical composition. In other words, the increase in light absorption is attributed to changes in polarizing power, modifier properties, coordination number, and the number of free oxygen functional groups in the polymer body [41]. Sample films were made by the spin coating process, in which a 1 cm diameter sample was taken and silver flashed on both sides of the film to ensure good contact for electrical measurements. The silver sample was placed between two similar brass electrodes in a spring-loaded sample holder.

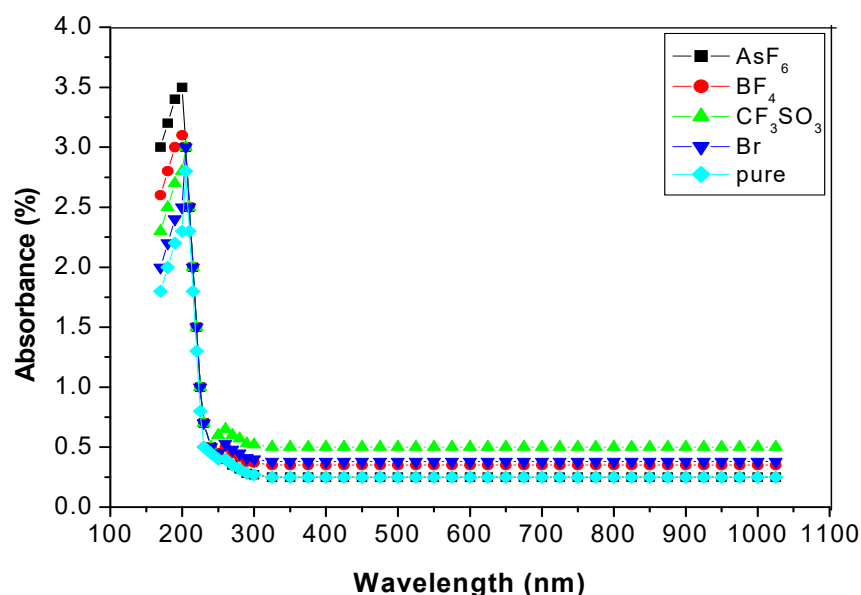


Figure 1. UV-vis absorption spectra of pure and Br, CF_3SO_3 , BF_4 and AsF_6 doped polymer films.

The entire assembly was placed in an oven controlled by a temperature controller. The heating rate was set at 2 K/min. Dielectric and electrical measurements were taken in the temperature range 300–500 K. Bulk samples for conductivity measurements were prepared by cutting crystals along cleavage planes, so the resulting surface was similar to a mirror without any mechanical treatment. It was then mounted on a cold finger inside a cryostat (Oxford model DN1704), which was evacuated to approximately 10^{-4} Torr. The temperature inside the cryostat was controlled by a digital temperature controller (Oxford model ITC601). The contact between the sample and the metallic electrodes was made by means of silver paste. The I-V characteristics of the electrical contacts were tested and found to be resistive over the range of applied voltages used. Conductivity measurements were taken using pulse excitation (a.c) and steady state (a.c) methods. The temperature remained constant.

3. Results and Discussion

Figure 1 shows the optical properties of different lithium salts that we used in PEO complexation to fabricate SPE, LiX (where $\text{X} = 1$ [pure], Br, CF_3SO_3 , BF_4 , AsF_6) membranes and solid polymer electrolytes. It can be seen that when AsF_6 is added there is a change in absorbance at longer wavelengths. It has also been documented that the AsF_6 -doped SPE polymer electrolyte film experiences a shift in absorption spectra at a wavelength higher

than the concentration. This change in absorbance correlated with a huge reduction of the ions into metal particles. It has also been linked to the efficient irradiation of polymer electrolytes. The effectiveness of irradiation on absorptive capacity (optical property) and electrical performance (ionic conductivity) for each of the blank and doped electrolyte films containing Br, CF₃SO₄, BF₄, and AsF₆, respectively, was also documented. It was observed that with an increasing radiation dose, the change in absorbance increases accordingly. Polymer electrolytes have also been considered to improve the performance of Li batteries due to their excellent properties regarding ion transport, similar to those of non-aqueous liquid electrolysis systems.

Figure 1 shows the optical properties of various lithium salts that we use in PEO complexation to fabricate SPE membranes, LiX (where X = 1 [pure], Br, CF₃SO₃, BF₄, AsF₆), and solid polymer electrolytes. It can be seen that the absorbance at longer wavelengths changes after the addition of AsF₆. It was also documented that AsF₆-doped SPE polymer electrolytic membranes undergo a shift in absorption spectrum at wavelengths above concentration. This change in absorption is associated with a substantial reduction of ions in metal particles. It is also related to the efficient irradiation of polymer electrolytes. The efficacy of radiation on the absorbance (optical properties) and electrical properties (ionic conductivity) of each of the bare and doped electrolytic membranes containing Br, CF₃SO₄, BF₄ and AsF₆, respectively, were also recorded. It was observed that as the radiation dose increased, the variation in extinction increased accordingly. Polymeric electrolytes are also considered to improve the performance of lithium batteries due to their excellent ion transport properties similar to non-aqueous liquid electrolysis systems.

The low leakage potential, flammability, and high energy density of polymer electrolytes have stimulated interest compared to conventional formulations. Polymer electrolytes generally consist of a lithium-based salt mixed with a polyether solvent. The main classifications of polymer electrolytes include polymer gel electrolytes and composite polymer electrolytes (CPEs). Polymeric electrolytes have been reported to act not only as electrolytes but also as submarines, avoiding dendrite formation, PS solubility issues, and safety concerns, due to their chemical stability. The lithium salt acts on the electrolyte, which has reached maximum conductivity, to achieve maximum conductivity. CH₂-CH₂-O is currently most commonly used in mixed carbonate solvents. It was also shown that the conductivity of the electrolyte containing CH₂-CH₂-O in the solvent mixture was significantly higher.

It can be clearly seen that the increase in the refractive index value correlates with the increase in the amount of SPE, as shown in Figure 2. Furthermore, all the doped films obtained a range of refractive index values in the range wavelength from 220 to 1100 nm. In fact, the increase in density is due to the increase in the AsF₆ content. It is important that the embedded sample shows characteristic peaks in the wavelength range between 650 and 750 nm. These peaks are the result of the interaction of incident light in the 570 to 980 nm range with AsF₆ surface plasmons. Furthermore, an increase in peak intensity was observed with an increasing amount of doping. These results confirm the presence of AsF₆ in the film.

Figure 3 shows the variation in the absorption coefficient for composite with various photon energy. The absorption coefficient (α) of composite depends on the optical absorbance (A) and thickness of the film (d), which is evaluated using the relation [42]:

$$\alpha = 2.303A/d \quad (1)$$

The optical energy gap (E_g) of the thin films was determined from absorption coefficient data as a function of photon energy. According to the generally accepted non-direct transition model for amorphous semiconductors proposed by Tauc [43],

$$\alpha h\nu = B(h\nu - E_g)^r \quad (2)$$

where B is a constant related to the properties of the valence band and conduction band, $h\nu$ is the energy of the photon, E_g is the band gap of the optical energy, $r = 2$ or 3 for the indirectly allowed and indirectly forbidden transition. From the linear plots of $(\alpha h\nu)^{1/r}$ versus $(h\nu)$, the optical energy band gap was determined from the intersection points of the zero extrapolations with the photon energy axis ($\alpha h\nu)^{1/r} \rightarrow 0$). From the results obtained, it can be observed that the reduction of the pure polymer and of the films doped with Br, CF_3SO_4 , BF_4 , AsF_6 , and the concentration of AsF_6 in the system, lead to a decrease in the optical bandgap. The increase in the bandgap with decreasing concentration may be due to the decreasing group size of the original solution. It was found that as the AsF_6 concentration decreased, the band edge shifted and the slope of the absorption spectrum changed, as shown in Figure 4.

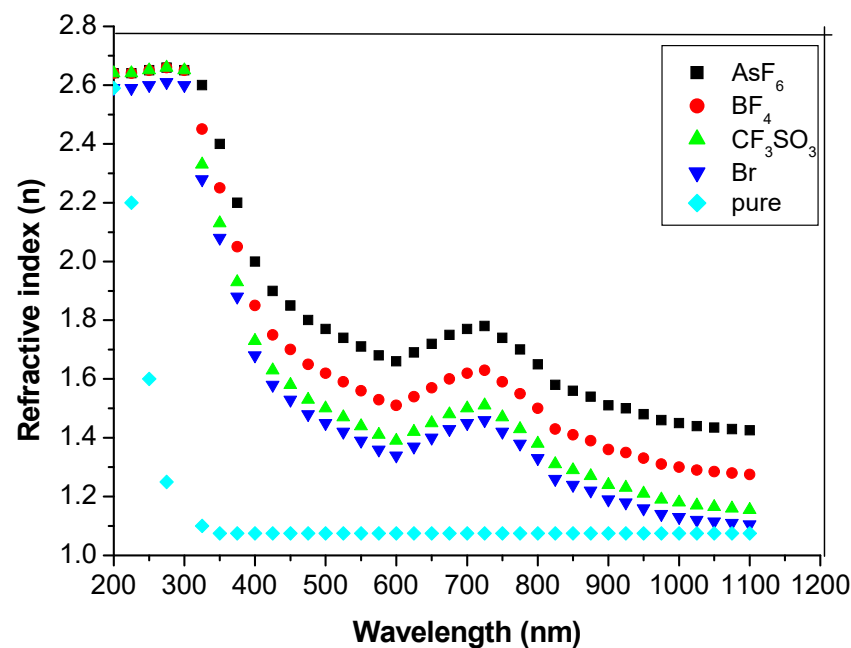


Figure 2. Pure and Br, CF_3SO_4 , BF_4 , and AsF_6 doped polymer films' refractive index.

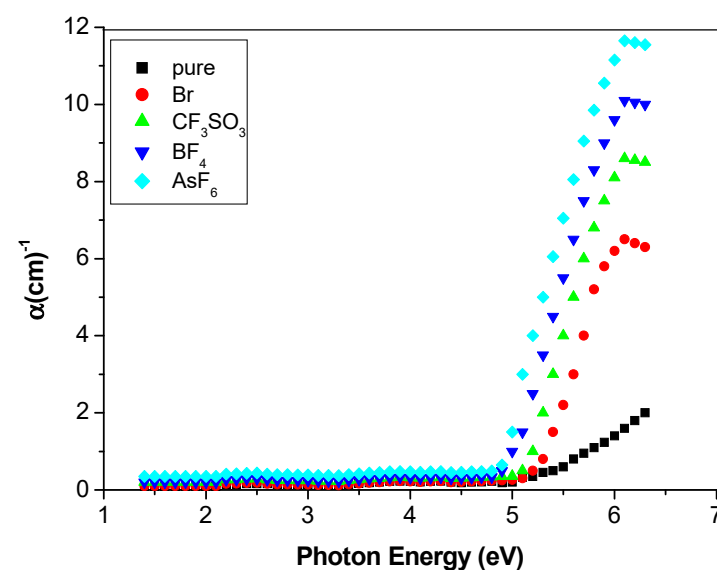


Figure 3. Absorption coefficient for composite with various photon energy.

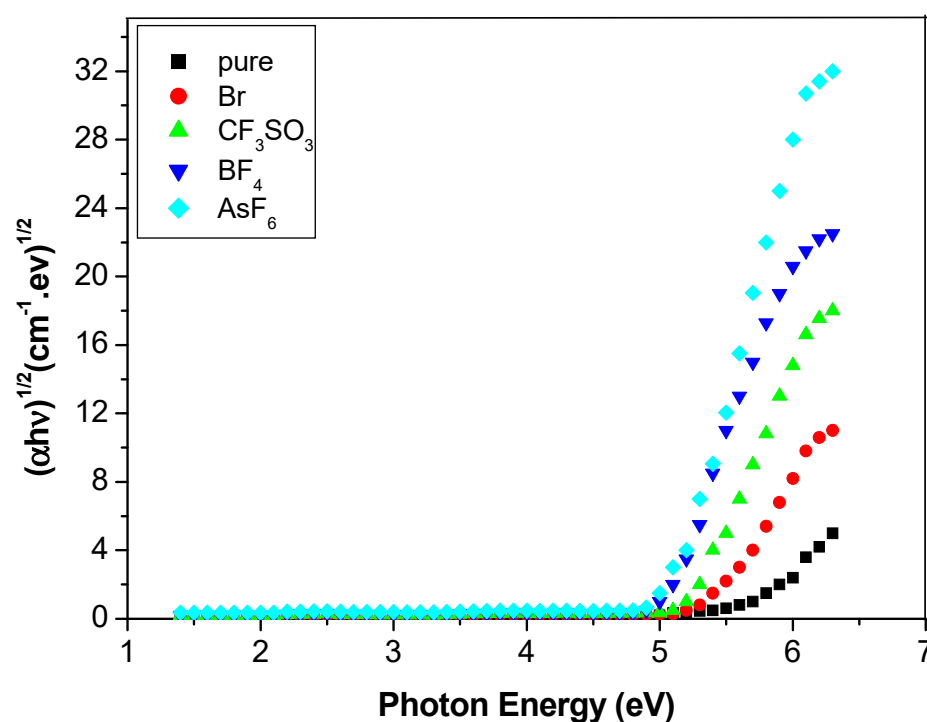


Figure 4. The relationship between $(\alpha h\nu)^{1/2}(\text{cm}^{-1}.\text{eV})^{1/2}$ and photon energy of composites.

The ionic conductivity values of the electrolytes are calculated by using Equation (3):

$$\sigma = l/Ra \quad (3)$$

where l and a are the known thickness and area of the electrolyte film, and R is the resistance of the electrolyte film at different AC frequencies. The conductivity of pure SPEs is equal to $\approx 5 \times 10^{-4} \text{ S cm}^{-1}$ and increases sharply to $\approx 2.1 \times 10^{-3} \text{ S cm}^{-1}$, and when doping with AsF_6 the conductivity becomes $\approx 7 \times 10^{-4} \text{ S cm}^{-1}$ and strongly increases a $\approx 2.4 \times 10^{-3} \text{ S cm}^{-1}$. Figure 5 shows the conductivity σ (zero frequency) as a function of the addition of Br-doped polymer films, CF_3SO_4 , BF_4 , and AsF_6 . It can be seen that the conductivity decreases as the AsF_6 addition increases up to 1.0 M, after which the conductivity increases. Crystallinity affects the conductivity of a sample. The amorphous nature produces a higher ion diffusivity, which corresponds to the high ionic conductivity that can be achieved with amorphous polymers with completely flexible structures [44]. We tried to explain the change in conductivity with Ag content by preparing films and adding different amounts of α to each solution. Therefore, the volume of the SPE host matrix was the same for all films. Two characteristic regions can be easily distinguished. Regions of a low initial concentration (I) where reduced conductivity was observed were attributed to ion pairing [45]. The subsequent linear region (II) showed an increase in conductivity beyond the minimum, possibly as a result of triplet ion formation or redissociation effects [45].

The conductivity of the PEO/Li salt system increased significantly with the addition of Li salts. This is because Li salts dissociate into Li^+ cations and anions in the PEO matrix, and the Li^+ cations become mobile in the polymer. The increased concentration of mobile ions in the PEO/Li salt system facilitate the transport of charge carriers, leading to enhanced electrical conductivity. Moreover, the PEO/Li salt system has some unique properties, including high ion conductivity, excellent stability, and low toxicity, which make it suitable for various applications, such as rechargeable batteries, fuel cells, and electrochromic devices. In summary, the addition of Li salts to PEO would increase its conductivity due to the presence of mobile ions in the system, leading to the enhanced transport of charge carriers.

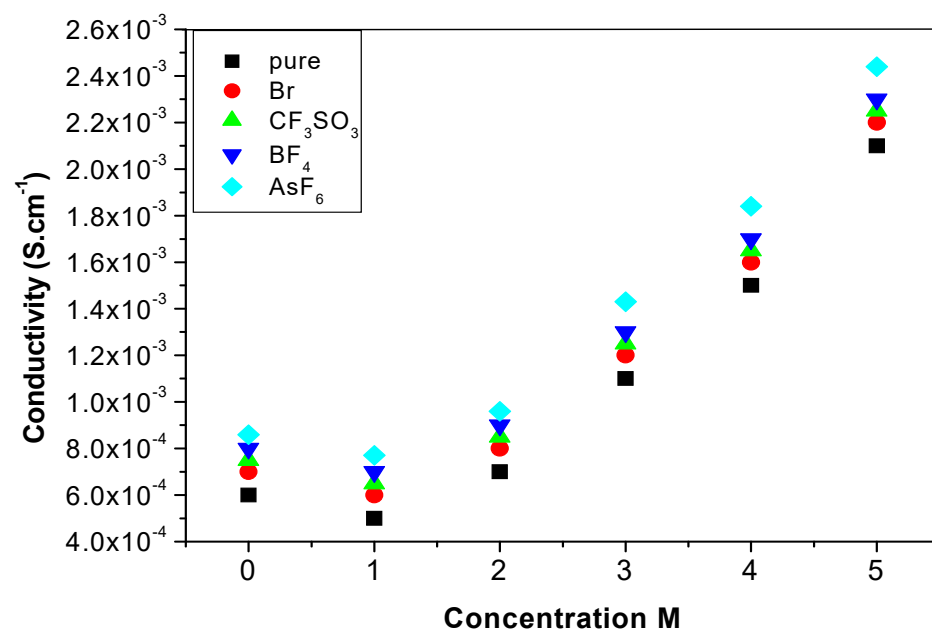


Figure 5. Concentration-dependent conductivity for pure and Br[−], CF₃SO₄, BF₄, and AsF₆ doped polymer films.

Figure 6 represents the temperature dependence of ionic conductivity for all compositions of SPEs. It has been found that the ionic conductivity of the membranes show two regions, the first at relatively low temperature. The ionic conductivity shows relatively temperature-independent behavior, while the second region indicates an Arrhenius-type thermally activated process given by Relation 4:

$$\sigma_{ac} = \sigma_0 \exp(-E_a/K_B T) \quad (4)$$

where σ_0 is the pre-exponential factor, E_a the activation energy and k is the Boltzmann constant. Druger et al. [46] attributed the increase in conductivity with temperature in solid polymer electrolytes to segmental (i.e., polymer chain) movement, which leads to an increase in the free volume of the system. Therefore, segmented motion allows ions to jump from one place to another or provides a path for ions to travel. In other words, the segmental movement of the polymer facilitates the translational ionic movement. From this it is clear that the ionic motion is due to the translational/hopping motion facilitated by the dynamic segmental motion of the polymer. As the amorphous region increases, the polymer chain adopts a faster internal mode, where bond rotation generates segmental motion, facilitating ion hopping between and within chains and thus, electrical conductivity increases.

It can be seen from Figure 7 that the dielectric constant of the SPE polymer electrolytic system increases with increasing temperature. This behavior is typical of polar dielectrics, where the alignment of the dipoles becomes easier with increasing temperature and thus the permittivity increases [47].

The frequency dependence of different values of ϵ' for Br, CF₃SO₄, BF₄ and AsF₆ doped polymer films in the SPE system at room temperature is shown in Figure 8. From the figure it is clear that the permittivity decreases monotonically with an increase in frequency and reaches a constant value at higher frequencies. Similar behavior was observed for other materials [48]. For polar materials, the initial value of the permittivity is high, but as the frequency of the electric field increases, this value begins to decrease, probably because the dipoles can no longer follow the change in permittivity at higher-frequency fields, and also due to polarization effects [47]. The scattered low-frequency range is attributed to charge accumulation at the electrode–electrolyte interface. At higher frequencies, the periodic reversal of the electric field occurs so rapidly that the ions do not scatter excessively in the direction of the electric field.

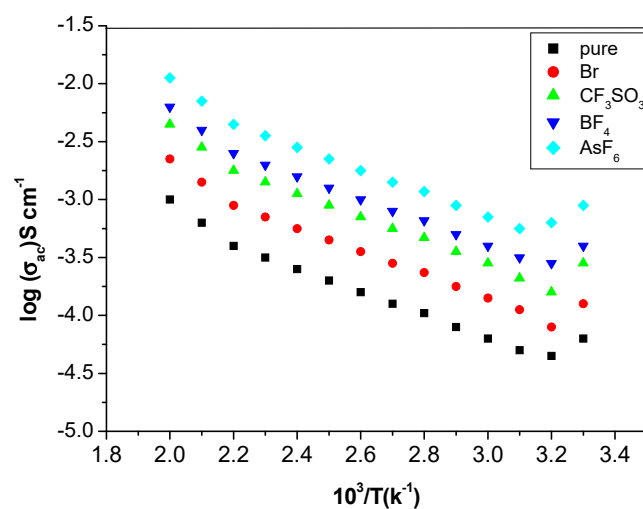


Figure 6. Temperature-dependent conductivity for pure and Br^- , CF_3SO_4 , BF_4 , and AsF_6 doped polymer films.

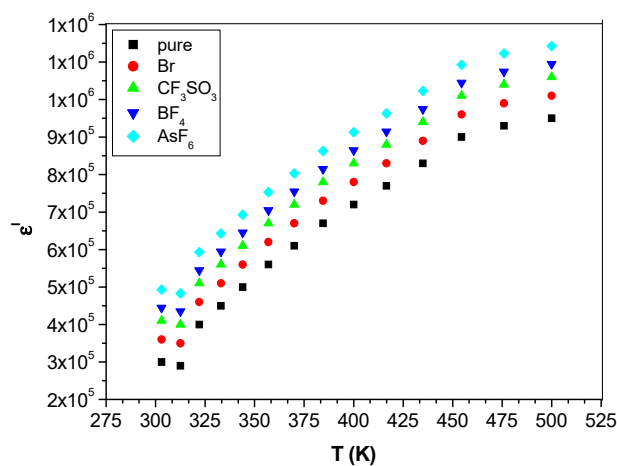


Figure 7. Variation of dielectric constant with temperature for pure and Br , CF_3SO_4 , BF_4 , and AsF_6 doped polymer films.

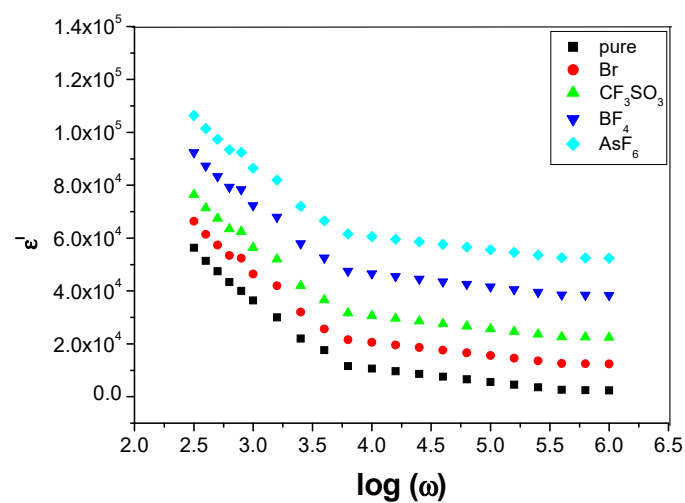


Figure 8. Variation of dielectric constant with frequency at temperature 303 K for pure and Br , CF_3SO_4 , BF_4 , and AsF_6 doped polymer films.

4. Conclusions

Recently, the application of polymers and compound electrolytes in various electrochemical, electrical and optoelectronic devices has improved. Different types of polymeric electrolytes have been studied and documented in the literature. The use of composite polymer electrolytes has been considered as a possible technique to exploit the performance of electrolytes. The optical parameters, the optical permittivity, the absorption coefficient and the refractive index were described. The optical band gap was studied using two methods: the Tauc model and the optical dielectric loss parameter. Based on a recently published work, a sufficient quantum mechanical basis was provided for the applicability of the optical dielectric loss parameters to the considered bandgaps. In this work, it was shown that it is necessary to study the Tauc model and the optical dielectric loss to specify the electronic transition modes and correctly estimate the optical band gap.

In green coordination chemistry, the preparation of polymers with desired optical band gaps is of great importance. Based on experimental and theoretical approaches, we found that the parameters of the optical dielectric loss should be investigated to specify the nature of the electronic transitions of the Tauc model.

The electrical and electrochemical properties of the solid acidic polymer electrolyte for SPE were improved due to the doping of Br, CF₃SO₃, BF₄, AsF₆; the electrical information obtained is summarized below. The ionic conductivity of the SPE electrolyte containing AsF₆ is $2.4 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. This solid acid polymer electrolyte can be used to make solid acid batteries.

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