

Ion-Conducting Composites of Polymers and Nematic Liquid Crystals

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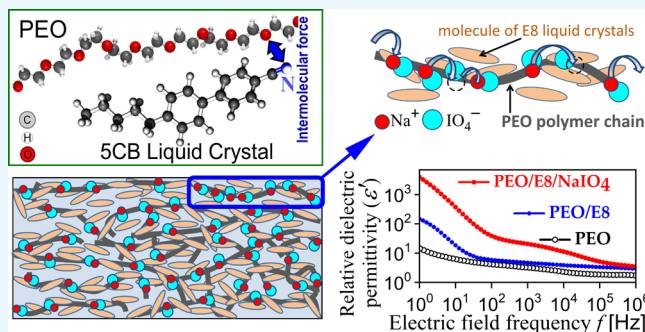
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ABSTRACT: In the present mini-review are discussed the findings reported in the last five years on the ion-conducting composites of polymers and molecules of nematic liquid crystals (NLCs), as well as their applications at present and in the future. Nowadays, free-standing and flexible thin films of such organic composite electrolytes synthesized from plastics and nematic soft matter are among the technically important materials and components for use in energy storage and conversion devices and in organic soft electronics, sensorics, and mechatronics. Although the physicochemical mechanisms and effects in the ion-conducting polymer/NLCs composites are well understood, the possibility to find additional ways for improving their electrical conductivity and dielectric and mechanical properties is a challenge. The efforts in this research direction are important for the development of novel ion-conductor materials and further diversification of their applications. This mini-review is focused on the key characteristics of ion-conducting polymer/NLCs composites and the new trends in their fabrication. With relevant examples, the vast research opportunities, some proposed improvements, and the creative ideas associated with these advanced materials and their intelligent use are outlined.



1. INTRODUCTION

In the past decade, various kinds of advanced multifunctional composite materials from polymers and liquid crystals (LCs) have been developed and thoroughly investigated due to their important properties.^{1–4} Such soft or soft-solid materials have found a wide variety of applications, the most popular being the electrically controllable large-scale screens, projection systems, 3D digital displays, light shutters, switchable windows, and energy-saving windows.^{1–4} The thermotropic LCs are mesogenic materials with different LC phases as a function of temperature. They combine the order of crystalline solids and the flowing properties of liquids. In particular, nematic LCs (NLCs) exhibit a nematic phase in a certain temperature range and represent a specific state of the soft condensed matter, with unique properties. Nowadays, dispersions of NLCs in polymer matrices are electro-optical materials fabricated to be used for thin films with electrically controllable light scattering. This effect is the physical basis of the polymer-dispersed liquid crystals (PDLCs) technology, well-developed at present. PDLCs comprise micrometer- and submicrometer-sized NLC droplets in a continuous polymer matrix. PDLC electro-optical thin films are currently employed for smart glasses, 3D displays, and tunable optical modulators, in flexible soft-matter photonics, diffractive and adaptive optics, lasers, sensors applications, and biomedical devices, for advanced anticounterfeiting, and in augmented and virtual reality, among others.^{2–6}

Besides PDLCs, another type of polymer/LC composite has been developed—the polymer-stabilized LC (PSLC).^{2,3,6} In contrast to PDLCs in which both the polymer and the LC phases are separated, in PSLCs a small amount of cross-linked polymer is dispersed in a continuous LC phase, and the LCs and polymer form an interpenetrating three-dimensional structure.

Following the practical demands, flexible and stretchable electroconductive polymer/NLCs composites (PNLCCs) have been intensively studied given their practical use in flexible displays, flexible organic electronics, sensorics, and mechatronics, as well as for rechargeable flexible batteries and wearable electronics.^{7–9} Room-temperature NLCs are attractive for producing ion-conductive materials due to the formation of the mesophase and their ionic conductivity. As is known, the NLCs have an elongated (almost rodlike) molecular structure configuration and, being extended dipoles, are highly polarizable in an external electromagnetic field. This makes them suitable components in soft or soft-solid composites with advanced

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multifunctional applications. In particular, very promising is the combination of the dipolar molecules of NLCs and polar polymeric materials in a composite.

Polar polymers contain polar groups (such as $-O-$, $-S-$, $-N-$, $=O$, $C=O$, and $C\equiv N$). These polymers are among the most promising and currently extensively investigated materials. Their combinations with NLCs have great potential in various dielectric, sensing, and biomedical applications and electro-optical devices, as well as in nonlinear optics (optical interconnections, telecommunications, and signal processing), adaptive optics, quantum electronics, and photonics, utilizing the molecular shape, molecular dipole moment, polarity and/or polarizability, dielectric anisotropy, and electrically controlled optical properties of NLCs. If the polar polymers are ionically conductive with a low electronic conductivity, they may be proper for fabrication of ion-conducting ion-polymer-coupled electrolytic systems, such as the alkali salt-complexed polymer electrolytes for rechargeable ion batteries and electrochemical cells widespread at present. Regarding the ionic electrolyte function, the polar polymers allow achievement of a better salvation of inorganic ionic salts (that are the ion donors), a higher polymer-ion coordination, and thus a higher ionic conductivity.

Further, some slightly polar or even nonpolar polymer structures that are electronically insulating but have electron-donating groups in the sequential repetition units in their chains may also dissolve ionic inorganic salts, followed by the complexation of the salts, appropriate for polymer-based ion electrolytic functionality. The imbalance of the distribution of electrons leads to a "polar" molecular character of such polymers, and in them dipoles are created. When subjected to an electric field, polymers containing active groups such as $-O-$, $-OH$, $C=O$, and $O-CH_3$ in their backbone behave as dipolar media and can be classified as "polar". They might also be suitable for polymer hosts for ion conductors. Commonly used polymer structures in ion-conducting polymer-based composites are poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(vinylpyrrolidone) (PVP), poly(vinylidene fluoride) (PVDF), poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), polycarbonate (PC), poly(vinyl chloride) (PVC), poly(vinyl cyanide) (PAN), polyamide (Nylon), chitosan (CS), polycaprolactone (PCL), and others. In recent years, polymer-LC composites gained a lot of attention directed toward the improvement of existing LCs-based technologies such as sensor and mechatronic systems, fabrication of new electronic devices, production of dielectric capacitors, and layering flexible conductive coverages, which expands the practical applications of both LCs and polymer materials.

In general, the interest in hybrid materials made of ion-conducting polymers and LCs has been triggered by the possibility of improving the ionic conductivity in solid or gel polymer electrolytes. The creative idea of using LCs as ion conductors in polymer electrolytes stems from the fact that LCs included in ion-conducting polymers can form ion-conducting channels that facilitate the ion transport through the polymer electrolytes. Interest in such complex ion-conducting plastic materials has risen rapidly since they have been proposed as polymer electrolytes for energy storage applications.¹⁰

Several research groups have synthesized diverse ion-conducting polymer-NLCs electrolytic materials, which have attracted reasonable research attention due to their electrical, dielectric, mechanical, thermal, and other properties valuable for

applications in the fields of electrochemical and ionic devices, organic electronics, sensorics, and mechatronics, as well as solar-cell organic photovoltaics.^{10–18} Presently, the engineering of ion-conducting PNLCCs is an important research field where the main focus of the research community is the search for new high-performance PNLCCs having interesting properties, great competitive advantages, and extensive application prospects.

This mini-review summarizes the results reported in the last five years from studies on ion-conducting PNLCCs related to the development of such composites for multifunctional applications. As suitable examples to illustrate this research topic, two ion-conducting PNLCCs based on the polymer PEO and NLCs E8 are considered herein. For both representatives, PEO/E8 and the salt-complexed ion-polymer-coupled system PEO/E8/NaIO₄ (polymer ion-conducting electrolyte), the compositional ratio PEO:E8 was the same (70:30 wt %) and found to be optimal for the physicochemical, ion conductivity, and dielectric properties of these composites, as well as for their good film-forming characteristics.^{16,17} The composite PEO/E8/NaIO₄ contains 10 wt % from the salt sodium metaperiodate (NaIO₄) as a dopant of Na⁺ ions (such concentration was found to be optimal, ensuring a fairly good ion conductivity and suitable dielectric permittivity without changing the other properties, quality, and long-term stability of this ion-conducting PNLCC).¹⁷ The two example composites may display the common characteristics of the ion-conducting PNLCCs. Comparison with other ion-conducting PNLCCs is given, along with the research progress on these polymer electrolytes. Their main application, as well as the research challenges and opportunities in this scientific area, are also pointed out.

2. ION-CONDUCTING PNLCCS: STRUCTURAL FEATURES

Polymer/nematic liquid-crystal composites (PNLCCs) are materials that enable combining the responsive characteristics of NLCs with the ion-conducting and film-forming properties as well as mechanical strength of polymers, e.g., synthetic polymers. The most prominent exemplarities from this class of multifunctional materials are the dispersions of NLCs in polymers, forming materials with two separated phases—the so-called PDLCs where well-formed micro- or nanosized NLC droplets take place as captured/capsulated within a solid polymer matrix.^{2,3,6} The dispersion of NLCs in polymers can also form guest-host molecular systems, blends, or other types of complex materials.^{9,18}

As viewed by optical microscopy, the PNLCCs usually display a mixed morphology that comprises optical textures of both the polymer phase and the liquid-crystalline nematic phase. In such hybrid textures, the morphological features and structural properties of PNLCCs strongly depend on the concentration of the NLCs. As an example, one can consider the structural properties of thin films made from the polymer poly(ethylene oxide) (PEO) and the room-temperature NLCs with the commercial name E8. The PEO/E8 ion-conducting dielectric composite material has attracted research interest because it exhibit properties useful for molecular electronics and soft-electronics applications.

The semicrystalline polymer PEO, $[CH_2-CH_2-O]_n$ (Figure 1 a), and its modifications have attracted much attention for a long time due to the highly flexible backbone at ambient temperature, the presence of an ether group supporting faster ionic transport, excellent electrochemical stability, good solubility with ionic alkali-metal salts, high dielectric constant,

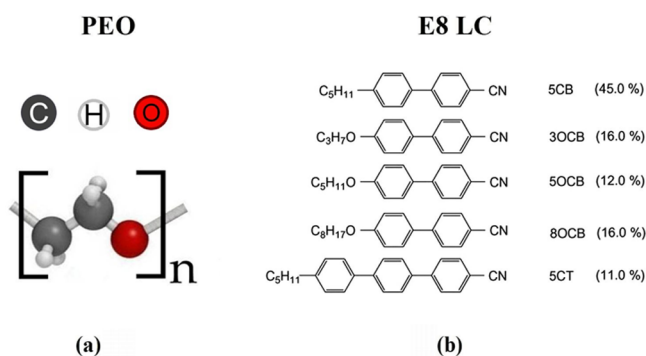


Figure 1. Molecular structures of poly(ethylene oxide) (PEO) (a) and the constituents of the NLC mixture E8 (b).

relatively low glass transition temperature (T_g), easy fabrication, low preparation cost, high safety, and other properties and characteristics desired and required for use in thin-film batteries, photovoltaics, and electrical engineering systems.¹⁹ Until now, PEO-based materials have been the main platform for fabrication of a number of compositions that have been applied as polymer electrolytes, in organic electronics and ionics, as well as in other science and technology fields. The charge-polarized group $-O-$ in the ethylene oxide (CH_2-CH_2O) repeat unit of the PEO polymer backbone makes this polymer polar (relatively weakly polar—the dipole moment of the PEO molecule is ~ 1 D, at 25°C). The polarity of PEO favors formation of PEO-based ion-conducting electrolyte materials. Efficient and reliable PEO–NLC ion-conducting systems have been reported.^{16,17,20}

The room-temperature NLC material E8 is an eutectic mixture of four cyanobiphenyl compounds: pentyl-cyanobiphenyl (5CB) and cyano-alkoxy-biphenyls (n OCB; $n = 3, 5,$ or 8), as well as pentyl-cyanoterphenyl (5CT), at a given composition (Figure 1 b). These five NLC compounds have positive and high dielectric anisotropy. The dielectric anisotropy of the nematic E8 is $\Delta\epsilon_a \sim 13$. E8 can maintain the nematic phase at room temperature until the temperature rises to nearly 70°C . The concentrations of the five NLC components in the mix E8 are specially optimized in order to design a high-performance NLC material with desirable properties for electro-optical device technology and applications, e.g., for LC-based electro-optical displays. The molecules of these compounds are small and elongated rodlike, polar, and with large dipole moments. For instance, the permanent electric dipole moment of the molecule 5CB, the main ingredient of E8, reaches 5 D. The electric dipolar properties of the NLCs should be taken into account, since they may strongly influence both electrical conductive and dielectric behaviors of ion-conducting PNLCCs.

2.1. Morphology. The dispersion and incorporation of NLCs in the bulk of the PNLCCs can be evidenced by polarizing optical microscopy. Figure 2b and c shows optical micrographs of a thin film of PEO/E8 composite.²¹ The presence of NLCs is visualized as a structure consisting of microsized LC domains. Such morphological textures are indicative of a complex polymer–NLC composite where the NLCs are in a confined geometry and the NLC phase is continuously incorporated in the host polymer matrix. Being captured in the bulk of the polymer PEO, microsized domains and multidomains of various sizes like clusters are relevant to the NLC phase of E8. These morphological features correspond to the bright textural objects observed by optical microscopy (Figure 2 b and c) Similar structural properties were reported for ion-conductive exem-

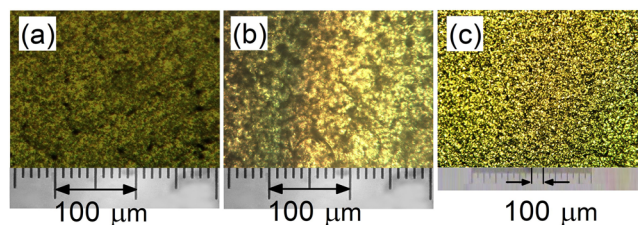


Figure 2. Optical micrographs taken at room temperature (25°C) for $150\ \mu\text{m}$ thin films of pure PEO (a) and PEO/E8 composite at 30 wt % concentration of NLC E8 (b, c). The samples were placed between slightly uncrossed analyzer and polarizer.²¹

plars of PNLCCs at room temperature, in particular for polymer ionic electrolytes with incorporated 5CB NLCs, e.g., by Said et al.¹² and by Kamarudin et al.¹⁵

When the liquid crystal concentration in the polymer is relatively high (e.g., 40–50 wt %), the microstructural morphology of PEO/E8 PNLCCs resembles that of the typical microscale PDLCs. In this case, distinct but randomly distributed NLC soft microdomains like droplets are formed in the 3D network of the polymer matrix.¹⁶ At a moderate concentration of NLCs (e.g., 30 wt %), in such a PNLCC structure one can see only the contours of LC droplets (Figure 2 b), which suggests that the LCs in the droplets are optically isotropic. Hence, this morphology strongly differs from the ordinary well-formed and well-separated (and in the perfect case—uniformly distributed) microdroplet structural organization of the NLC phase within the bulk of the PDLC materials obtained by thermally- or photoinduced phase-separation processes.^{2,3,6} If viewed at lower magnification, the PNLCCs considered here may display a relatively homogeneous texture (Figure 2 c). Upon heating, the morphology of PNLCCs can undergo significant change, especially above their glass-transition temperature and close to their melting point,²² which is reasonable.

Micrographs of PNLCCs at a higher spatial resolution, obtained by scanning electron microscopy (SEM), have displayed a complex 3D morphology. Figure 3a shows a cross-

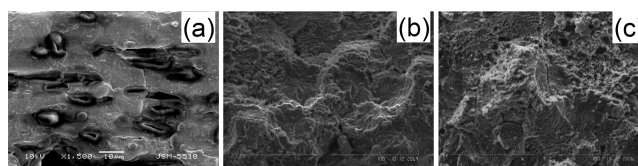


Figure 3. SEM images of cross-sectional morphologies of $150\ \mu\text{m}$ thin films of PEO (a), PEO/E8 (w/w = 70/30%) (b), and PEO/E8/ NaIO_4 (w/w/w = 63/27/10%) (c). Micrographs obtained at ambient temperature by use of inspection instruments JEOL JSM-5510 (a) and JEOL JSM-T200 (b, c).

sectional view of a $150\ \mu\text{m}$ thick film of PEO prepared by solution-casting technique. The inclusion of E8 liquid crystals at a relatively high concentration does significantly modify the microporous structure of this semicrystalline polymer. As an example, Figure 3 presents SEM images taken for films of PEO/E8 (Figure 3 b) and PEO/E8/ NaIO_4 (Figure 3 c). These PNLCCs were prepared in an identical way with the solution-casting method. As seen from Figure 3, the relatively large voids (sizes $\geq 10\ \mu\text{m}$) in the bulk of the PEO film become much smaller by the addition of E8 NLCs at 30 wt %. Actually, the microvoids are replaced with a fine porous spongelike random

structure (pore size of approximately 1 μm and less). Such a “densifying and smoothing” structural effect for the host polymer and obtaining a more homogenized material are known to occur by blending of PEO with a suitable organic component plasticizer. In fact, this has been observed for 150 μm thick composite films produced by solution casting from PEO blended with the amorphous polymer poly(vinylpyrrolidone) (PVP) at a weight fraction of 30 wt %.²³ Thus, the SEM observations in Figure 3 suggest that the material formed in the considered PNLCCs possesses a higher degree of amorphousness than the polymer PEO itself. In these structures inspected by SEM, one could not identify specific assemblies or aggregation forms, e.g., such as NLC molecular agglomerates whose formation may be promoted from cyanophenyl molecules of E8 LC being in a confined volume within the host polymer (confined in the nanoscale vicinity to the PEO functional groups).²⁴

The structural changes resulting from the NLC molecules dispersed into the polymer can be evidenced by vibrational spectroscopy (micro-Raman and FT-IR absorption). The data obtained by these spectroscopy techniques reveal the successful inclusion of the nematic in the bulk of the PNLCCs, as well as the resultant increase of the relative content of the amorphous phase in the inspected ion-conducting PNLCCs after the inclusion of NLCs.^{16,17} The latter effect can be well established by thermal studies, such as differential scanning calorimetry.^{16,17}

2.2. Intermolecular Interaction. If the structural units of the host polymer contain polar functional groups, one may expect electrical dipolar interactions between the dipolar molecules of the included NLC molecules with the polymer chains. This remarkable peculiarity is worth noting. The dipole–dipole (electrostatic) interaction between the polymer chain segments and the NLC molecules can lead to complex intermolecular formations like coupled electrical dipoles. This happens during the process of the synthesis/polymerization of PNLCCs. In particular, in PEO/E8, such dipolar molecular configurations may be formed from NLC molecules coupled to the ether oxygens in the C–O–C subunits of PEO (Figure 4).^{20,22} In this case, the electric dipole–dipole interactions

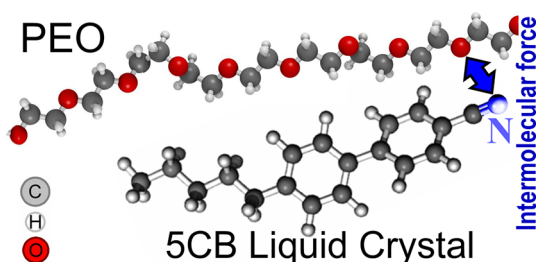


Figure 4. Intermolecular force induced coupling of the 5CB molecule to the molecular structure of PEO.

between the NLCs and the polymer PEO arise because the cyanocompounds in E8 have highly polarized terminal cyanogroups (due to the triple $-\text{C}\equiv\text{N}$ bond) and easily polarizable biphenyl groups. The role of the intermolecular forces induced in this way was also highlighted by Liu and co-workers⁹ for the recently developed composites from NLCs 5CB and the polymer poly(vinylidene fluoride) (PVDF).

Other types of intermolecular interaction between NLCs and polymer hosts are also possible, depending on the molecular

structures and properties of these two constituents of PNLCCs. In particular, as discussed by Said et al.¹³ in the case of ion-conducting PNLCCs from polymer poly(vinyl alcohol) (PVA) and the NLCs 5CB, the polymer–NLCs interaction is primarily due to the electron–hole pairs in PVA induced from the polar 5CB molecules. Furthermore, the NLC molecules can interact with the polymer segments through their surface.^{12,13,22} For that, a significant role is played by the anchoring-like interface effects and, accordingly, the anchoring properties of NLCs.

Information on the structural modification of the host polymer due to the inclusion of NLCs can be obtained by microstructural investigations. The formation of intermolecular dipoles in PNLCCs can be evidenced by means of structure characterization methods such as X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Besides the phase composition and the influence of the nematic on the crystalline status of the host polymer, the analyses of XRD and XPS data might be indicative of the intermolecular interaction between the polymer chains and the NLCs in the PNLCCs. In particular, XPS studies on PEO/E8 at various concentrations of the E8 NLCs suggest some type of molecular coupling in these PNLCCs formed through interactions between CN-biphenyls of E8 and the ethylene oxide ($\text{CH}_2-\text{CH}_2\text{O}$) units of the polymer PEO.²⁴ Furthermore, analyses of XRD patterns observed for PEO/E8 composites by increasing the percentage of E8 NLCs (e.g., in the range 10–50 wt %) reveal a structure different from that of the original structure of PEO.²² In this case, the additional diffraction peak registered at a higher percentage of NLCs can be attributed to intermolecular structural formation promoted from the cyanophenyl NLC molecules of E8.²² Results obtained by optical spectroscopy (vibrational spectroscopy: Raman and FT-IR absorption^{16,17}), as well as by analysis of thermal behaviors of PNLCCs,²⁰ also suggest an interaction of the dispersed NLCs with the polymer in the PNLCCs.

2.3. Orientational State. The nanoconfinement of NLCs into the bulk of PNLCCs and the chaotic coupling of the NLC molecules to the 3D polymer network due to dipole–dipole interactions strongly restrict the orientational order and impede the NLC orientation by an external electromagnetic field. Remember, the field-driven orientation effect is the physical mechanism of the operation of the PDLC electro-optical films.^{1–3,6} The simple control of the optical transparency of the PDLC devices by an applied electric field with relatively low voltage is based on the field-induced orientation of the NLC molecules in the droplets (where the NLC material is in a fluidlike state) dispersed/dispersed in the bulk of PDLCs. Such alignment of NLC electrical dipoles happens due to the dielectric anisotropy ($\Delta\epsilon_a$) of the NLC molecules in the droplets. If the NLC dipolar molecules have a positive dielectric anisotropy (which is the case for E8 NLCs), then they may be oriented along the direction of the applied field if the field intensity is high enough.

Unfortunately, such an effect upon the electric field is impossible in the ion-conducting PNLCCs with dispersed NLC molecules considered here. No structural anisotropy, and hence no conductivity anisotropy, can be electrically induced in them, and the NLC molecules in the host polymer remain with their random orientations. Also, the eventual field-driven reorientation of the LC molecules within the nematic microdomains disposed in the bulk of PNLCCs (such as those seen in Figure 2 b and c) is hampered because the two phases (polymer and LC nematic) are not fully separated in the considered PNLCCs

(composed from molecular NLC materials) that have been simply prepared only by mixing of the monomer mass and NLCs without the application of a method for the alignment of NLC molecules. The lack of electroactive properties has been evidenced by optical polarization microscopy studies of PNLCCs under an electric field.²²

In practical terms, unless suitable conditions are imposed a priori, e.g., special treatment of the substrate surface(s) of the PNLCC film, no initial orientation of NLC molecules in such PNLCCs can be expected. Thus, the spatial orientation of the dispersed NLC molecules is random; normally they are not ordered nor may their orientation have a predominant direction. Still, by chemical treatment and/or special molecular design of PNLCCs (e.g., induced alignment controlled by use of alignment layers on the substrate or by applying an electric field), the orientational order of NLC molecular dipoles in PNLCCs can be achieved, and this may generate anisotropy of the ion conductivity. Such an approach was demonstrated in a study carried out by Kamarudin et al.¹⁴ using a mixture of NLCs and smectic LCs in polymer electrolytes.

It should be noted that for ion-conducting PNLCCs, such an orientation effect is weaker than that achieved by composite polymer electrolytes designed by use of some ionic LCs²⁵ and much weaker compared to the well-known ordering in the polymer electrolytes with included discotic LCs forming columnar LC phases. An oriented arrangement of NLC molecules dispersed in the ion-conducting PNLCCs considered here, and hence the formation of the oriented ion-conductive pathways between electrodes, is principally possible but hardly realized. In any case, the NLC molecules can provide a better pathway for active ions inside the PNLCCs, thus contributing to the ionic transport in these complex electrolyte systems.

3. KEY CHARACTERISTICS OF ION-CONDUCTING PNLCCS

3.1. Ion-Conducting Properties of PNLCCs. Generally, the nematics are ion-conductive media, weakly conducting dielectrics. In the bulk of the nematic materials, there is always a small amount of certain free ions due to impurities in the NLC compounds during their synthesis. Even though commercial NLC mixtures are extensively cleaned of ions, such contaminating mobile ions contribute to the conductivity of the NLCs. Actually, the bulk nematics exhibit a relatively small electrical conductivity in the range of 10^{-12} – 10^{-14} S·cm⁻¹. In a capacitor-like geometry, the electrical conductivity of these media becomes higher due to a charge injection from the cell electrodes upon an applied electric field. This can induce ion migration from the electrodes into the bulk of the nematic medium, and thereby its effective ion conductivity is enhanced. Dispersed in polymers, the NLCs retain their electroconducting properties. If the host polymeric material is an ion-conducting dielectric and exhibits an electrical conductivity that is higher than that of nematics, the inclusion of NLCs into such a polymer may still modify its electrical and dielectric properties. Reasonably, this effect depends on the concentration of the NLC component of the PNLCCs.

As a representative example for such a host for PNLCCs, the polymer PEO can be considered. So far, now, PEO and its modifications are still the main candidates for polymer host materials in polymer-based electrolytes. This is because PEO has a high dielectric constant, strong solvating ability for the mostly used alkali metal ions, and good chain flexibility. At ambient temperatures, the electrical conductivity of PEO is relatively low

(10^{-9} – 10^{-8} S·cm⁻¹) due to the high crystallinity of this polymer. The active ionic species in pure PEO are the H⁺/OH⁻ ions. Upon application of an electric field, these ions are transported along PEO chains via the ether oxygen atoms exploiting local segmental motions of the polymer. The charge carrier migration in PEO is described by a hopping process. As is known, unbonded hydroxide (OH⁻) ions are involved in the conduction process in pure PEO (the charges in PEO are mainly negative mobile and positive stationary).

By inclusion of donors of ions (e.g., ionic compounds of alkali metals) in PEO, as is the case in PEO-based high-performance metal–ion salt-complexed polymer electrolytes,^{19a–f} owing to the specific physicochemical properties of PEO this polymer enables the dissolving of ionic salts added at relatively high concentrations. This occurs due to a favorable arrangement for efficient interaction with alkali-metal cations, which results in their complexation with the oxygen entities in PEO. The coordination complexes formed from the ether oxygen in the backbone of PEO and the metal ion cause a dissociation of the anions and cations of the added salt. In the presence of an applied external electric field, the cations can move from one coordination point to another by the mechanism of ion hopping or migration²⁶ (Figure 5). The polymer host supports the

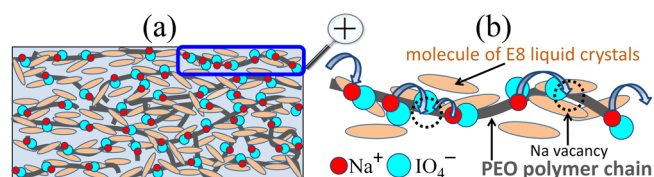


Figure 5. Schematic illustrations of the structure of PEO/E8/NaIO₄ (a) and the hopping conduction of Na⁺ ion based on a series of hopping within the structural segments of this PNLCC (b).

movement of the working ions by providing free space volume, as well as by segmental motion of the polymer backbone. It is well-known that the ion conduction occurs mainly in the amorphous phases in PEO.²⁶ The inter- and intrachain ion hopping occurs between coordinating sites. In the case of PEO/E8/NaIO₄, the Na⁺ ions are coordinated by ether oxygen atoms of the PEO chains and move via the coupling/decoupling of Na-to-oxygen bonds; i.e., Na⁺ ions can migrate from one site to another without the aid of the segmental motion.

3.1.1. Impedimetric Response and Dielectric Relaxation Behavior. In contrast to the ionic compounds such as the inorganic ionic salts of alkali metals dissolved in polymers like PEO or in suitable polymer blends, the NLC dipolar molecules in PNLCCs are not decomposed and cannot provide decoupled (free) electrical charges (ions) able to migrate. In this sense, the NLCs stay electrically inactive, being “anchored” to the structural units of the polymer chains and thus “decorating” them. Still, the polar molecules of NLCs included in the polar polymers, as well as the possible electrostatic attractions between NLCs and the polymer structural units (and thereby the intermolecular dipole structures eventually formed in PNLCCs, as discussed in Section 2.2), can considerably affect the electrical properties of ion-conducting PNLCCs.

As an example, Figure 6a reports data obtained by complex electrical impedance spectroscopy (EIS) for real (*Z'*) and imaginary (*Z''*) parts of the complex electrical impedance $Z^* = Z' + iZ''$ of thin films of PEO, E8, and PEO/E8 (70/30 wt %) composite, measured under identical experimental conditions as

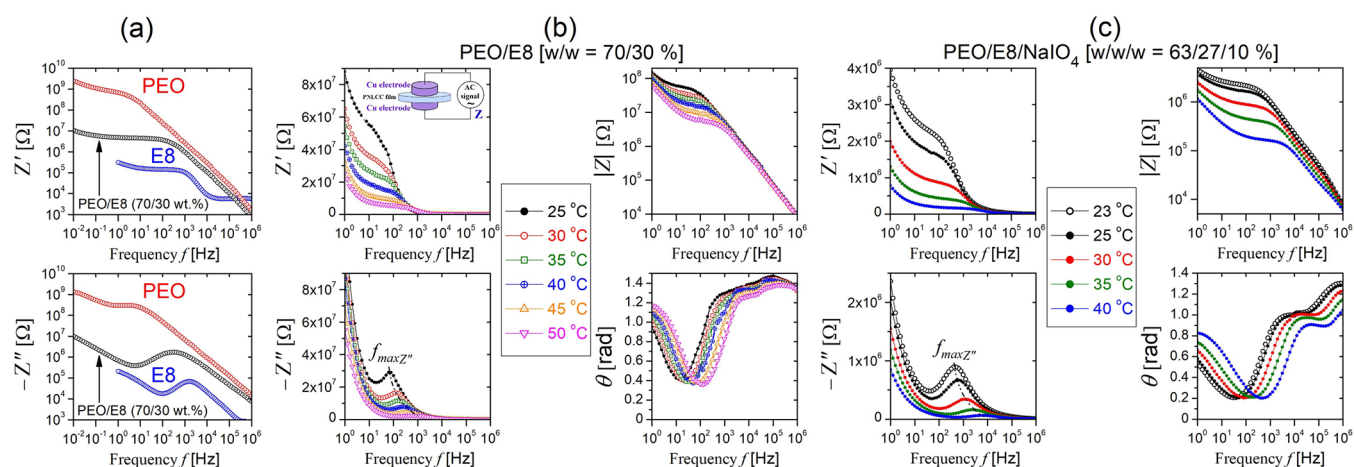


Figure 6. (a) Comparison of frequency spectra of the real (Z') and imaginary (Z'') part of the complex electrical impedance of thin films of PEO (150 μm thickness), E8 NLC (25 μm thin), and PEO/E8 (w/w = 70/30%) composite (150 μm thin) measured under identical experimental conditions at 26 $^{\circ}\text{C}$. Frequency-dependent Z' and Z'' , the modulus $|Z|$, and the phase θ of complex electrical impedance of PEO/E8 (b) and PEO/E8/NaIO₄ (c) ion-conducting PNLCCs at various temperatures. Inset in (b): the EIS measurement scheme.

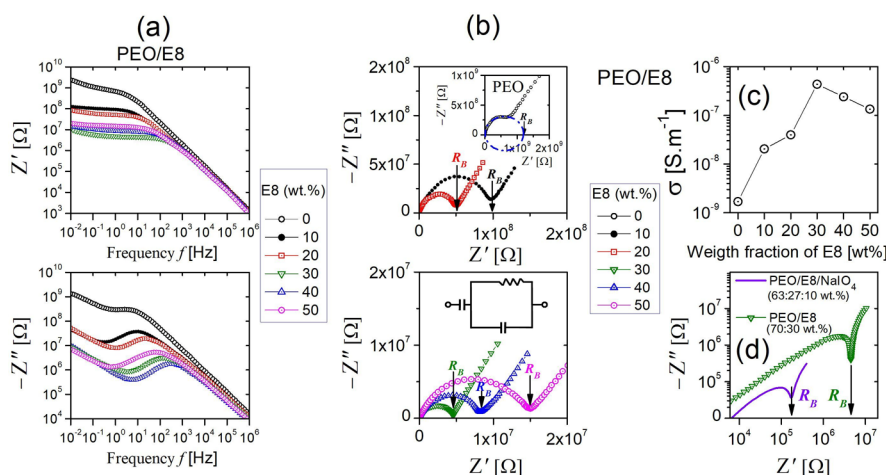


Figure 7. Frequency spectra of complex electrical impedance Z (a), Nyquist plots (b), and ion conductivity σ (c) of 150 μm thin films of PEO/E8 composite at various concentrations of the included NLC E8 (at room temperature, 26 $^{\circ}\text{C}$). The insets in (b) shows the Nyquist plot obtained for a 150 μm thin film of pure PEO and equivalent electrical circuit corresponding to the measured Nyquist plots. (d) Comparison between Nyquist plots of 150 μm thin films of PEO/E8 (w/w = 70/30%) and PEO/E8/NaIO₄ (w/w/w = 63/27/10%) measured under identical experimental conditions at temperature 30 $^{\circ}\text{C}$.

a function of the frequency f of the alternating-current (AC) electric field applied to the films. The maximum of Z'' is relevant to the main dielectric-active relaxation in the dielectric materials (in the particular cases: PEO, E8, and PEO/E8) upon external AC electric field (i.e., by induced electric polarization). The frequency $f_{\text{max}Z''}$ corresponding to the Z'' peak is known as the relaxation frequency of the dielectric medium. This key characteristic expresses the characteristic relaxation time $\tau = (2\pi f_{\text{max}Z''})^{-1}$ of the medium. In general, one can accept that the Z'' peak originates from the orientation of dipoles (dielectric relaxation of the orientational electric dipole polarization). Figure 6a shows that the effect from the inclusion of E8 LC molecules into PEO polymer can be significant. As a result, the impedimetric and dielectric relaxation behaviors of PNLCCs appear as intermediate between those of the polymer and the corresponding bulk NLCs.

The dielectric relaxation behaviors of PNLCCs (such as PEO/E8 considered here as an example) under an AC electric field are typical characteristics of the process of field-induced

reorganization of dipolar molecular formations (dipole polarization). According to the conventional and novel approaches toward understanding electrical transport phenomena in ion-conductive polymer-based systems and electrolytes,^{26,27} they are media with dipolar character of molecular interaction. In fact, the results from analyses of EIS data reported in several studies^{16,17,20} support the model of dipolar molecular organization and dipole–dipole interaction in the ion-conducting PNLCCs. For such composite dielectric materials, the dielectric relaxation upon an external AC field applied to them is defined by the responses of both their constituents: the ion-transporting polymer and the NLC soft matter. For that, the possible formations of coupled intermolecular dipoles in PNLCCs due to electric dipole–dipole interaction between the dispersed NLC molecules and functional groups in the polymer structural units may influence the dielectric relaxation processes in PNLCCs. Due to the flexibility of the polymer chains, local motions of the NLC–polymer intermolecular dipolar formations are possible, and the NLC dipole molecules

Table 1. Room-Temperature Ionic Conductivity (σ) Values Reported for Some Salt–Polymer Ion-Conducting Systems: Ion-Conducting PNLCCs (a); Polymer-Blend Ion Composite Electrolytes (b); Polymer Systems Containing Alkali-Metal Salt Structures and Ionic Liquid Crystals (ILCs) (c), or Ionic Liquids (ILs) (d)

ion-conducting system	composition	conductive ions	σ (S·cm ⁻¹)	ref
(a) PNLCCs	weight percentage, [w/w/w], (wt %)			
PVA/SCB/KI	[47/28/25]	K ⁺	1.4×10^{-3} (30 °C)	12, 13
PEO/E8/NaIO ₄	[63/27/10]	Na ⁺	1×10^{-7} (30 °C)	17
PEGDE/C6M/LiTFSI	[30/61/9]	Li ⁺	6×10^{-5} (30 °C)	18
(b) (polymer blend) ion electrolytes				
(PEO/PVP)/NaIO ₄	[63/27/10]	Na ⁺	1.5×10^{-7} (30 °C)	32a
(PEO/PVA)/NaIO ₄	[40/40/20]	Na ⁺	1×10^{-7} (30 °C)	32b
(PEO/PVP)/NaCl	[62.5/22.5/15]	Na ⁺	1.6×10^{-7} (30 °C)	32c
(PEO/PVP)/NaNO ₃	[67/27/6]	Na ⁺	6.1×10^{-7} (30 °C)	32d
(PEO/PAN)/NaClO ₄	[79.2/8.8/12]	Na ⁺	2.1×10^{-6} (R.T.)	32e
(PEO/PVP)/LiBr	[28.8/67.2/4]	Li ⁺	1.6×10^{-6} (30 °C)	32f
(c) ILCs-containing polymer electrolytes	[weight ratio]			
PEGDA/ILC/PEGDE/LiBF ₄	PEGDA/ILC/PEGDE = [4:1:16] [EO]:[Li] = 7	Li ⁺	2×10^{-4} (30 °C)	25a
PEO/PLA/LCI/LiClO ₄	[50:50:0.5:12]	Li ⁺	2.2×10^{-4} (17 °C)	25b
(d) IL-containing polymer electrolytes	weight percentage, [w/w/w], (wt %)			
PEO/(EMIm-TCM)/NaI	[87/(8)/5]	Na ⁺	4.2×10^{-5} (25 °C)	33a
PVDF-HFP/NaTf/(PMII)	[42/18/(40)]	Na ⁺	1.3×10^{-3} (30 °C)	33b
PVDF-HFP/NaTf/(BMImTf)	[56/24/(20)]	Na ⁺	1×10^{-3} (30 °C)	33b
PEO/LiTFSI/(PYR ₁₃ FSI)/EC	[34/11.1/47.5/(7.4)]	Li ⁺	1.6×10^{-3} (20 °C)	33c
PEO/LiFSI/([EMIM][FSI])	[72.5/20/(7.5)]	Li ⁺	2.9×10^{-4} (R.T.)	33d

participate together with the polymer backbone in the polymer chain motion. Thus, the coupled NLC–polymer dipolar formations can be involved in the dielectric relaxations in the PNLCCs upon an externally applied AC electric field. The oscillating electric field can cause the dipoles in such complex dielectric material to align, resulting in polarization. As recently reported, this can be evidenced by analyses of the thermodynamical behaviors of the PNLCCs.²⁰

At a higher temperature, the characteristic dielectric relaxation frequency $f_{\max Z''}$ of ion-conducting PNLCCs is increased (Figure 6 b) because of the increase in the segmental motion of the polymer. The same applies to ion-doped PNLCCs (ion–polymer electrolytes), e.g., metal–ion salt-complexed PNLCCs synthesized by the addition of the ionic salt of an alkali metal, such as the ionic inorganic compound sodium metaperiodate (NaIO₄) as a donor of Na⁺ ions (Figure 6 c). For such ion-conducting PNLCCs where metal ions are active for the ion transport, the same conclusions from impedance studies may be drawn, regarding the presence of molecular dipoles, dipole polarization (dipolar reorganization), and dipole relaxation (dielectric relaxation of dipoles) driven by an external AC electric field. Significantly, in this case the value of $f_{\max Z''}$ is higher, and the characteristic dielectric relaxation time is shorter, as compared to the corresponding undoped (base) ion-conducting PNLCCs (Figure 6 b and c).²⁰ This is explained with the structural changes induced by the ion donor, mainly the increase of the amorphous portion in the PNLCC material and, thereby, the increase in the segmental motion of polymer chains due to the addition of the salt.^{17,22}

3.1.2. Ionic Conductivity. In a number of works, it has been reported that the NLCs dispersed of PNLCCs lead to enhanced ion electrolytic properties.^{10–14,16,20} In particular, Figure 5 presents the results obtained for ion conductivity (σ) of PEO/E8 composite thin films measured by EIS. The shape of the Nyquist plots ($-Z''(f)$ vs $Z'(f)$) shown in Figure 7b is typical for such ion-conducting dielectrics. In this case, the complex diagrams consist of a part of a semicircular arc on the high-

frequency side, followed by a steep line (forming an inclined spike) at the low-frequency side. The semicircle corresponds to the bulk electroconducting properties of the sample. In the low-frequency region, the steep increase of Nyquist plots as the frequency decreases is relevant to a buildup of electric double-layer capacitance at the electrode/sample interface (a phenomenon known as the electrode polarization effect of accumulated interfacial charges and permanently induced polarization). The value of the ion conductivity (σ) of a planar film measured in a plane-parallel capacitor geometry (between parallel plane electrodes) is determined according to the expression $\sigma = d/(R_B A)$, where d and A are the thickness and the electrically active area of the film, respectively. The value of the bulk resistance (R_B) of the film is determined from the point of interception of the low-frequency end of the semicircle with the Z' -axis.

As seen from Figure 7b and c, the inclusion of the NLC E8 leads to a considerably higher σ . Furthermore, a linear increase of the concentration of the nematic up to 30 wt % results in an increase of the value of σ of the PNLCC PEO/E8 with more than 2 orders of magnitude. This means that although the NLC component is ion-conducting, the contribution of only its own conductivity to the total ionic conductivity of the PNLCC is not the most essential factor for enhancing the ion conductivity. Indeed, the σ increment vs the increment in the concentration of E8 is much higher than that expected from the simple multiplication of the net conductivity of this NLC. Therefore, the NLCs are actively involved in ion transport in PNLCCs, and a synergy effect is obtained.

It is clear that in ion-doped PNLCCs their conductivity due to ions donated from the included ionic compounds should be higher as compared to the undoped case. As a representative example, Figure 7d compares the impedimetric responses of PEO/E8/NaIO₄ salt-complexed PNLCC (ion–polymer-coupled electrolyte system) and PEO/E8. Both materials were measured in a flat-parallel capacitor-like geometry upon application of an AC electric field. From the reduction of the

bulk resistance R_B , one can calculate that at the concentration of 10 wt % of NaIO_4 included in the PEO–E8 mix during the synthesis of PEO/E8/ NaIO_4 , this Na^+ -ion transporter exhibits an ion conductivity that is higher by 1 order of magnitude than the conductivity of PEO/E8 at the same PEO:E8 wt % compositional ratio. The Na^+ -ion conductivity in PEO/E8/ NaIO_4 is supported by the additional increase of the amorphous phase of the polymer host due to the interaction of the ion-donor compound with the polymer network.^{17,22}

Typically, the considered PNLCCs exhibit relatively low ionic conductivities of only 10^{-6} – 10^{-7} $\text{S}\cdot\text{cm}^{-1}$ at room temperature due to the limited ion transportation via the segmental motion of the polymer backbone. As such, their ion-conducting ability may be comparable to that of the salt-complexed polymer (or polymer-blend) electrolytes. For some of the ion-conducting PNLCC composites discussed here (containing molecular NLC materials), the value of the room-temperature ionic conductivity can reach 10^{-3} S/cm ^{12–14} (Table 1). Such conductivity values are relatively high, only 1 order of magnitude lower than the commercial liquid electrolyte solutions, and are comparable to those reported for some ionic liquid crystals (ILCs)-containing polymer electrolytes or composite ILC electrolytes^{25,28} ion conductors synthesized from specific monomers and ionic liquids (ILs),^{29,30} as well as from polymers, ILCs, and ILs.³¹ The ion transport in all these systems has specific features.

On the other hand, the ion-conducting ability of polymer electrolytes composed from ILCs or ILs is determined from the resulting all-organic structure that can provide ordered ion-conductive pathways for highly efficient ion transportation, resulting in a significant increase in ion conductivity.^{25,28,29} Moreover, the ionic conductivity in such systems can be enhanced by means of a tailored design of ILC and IL molecules thus providing additional regulated multidimensional ion-conductive channels for migration of the working ions. Thus, in general, these systems exhibit higher ion conductivities than the PNLCCs discussed here. Still, it is worth emphasizing that the advantage of the PNLCCs that is the object of the present mini-review is their high stability at room temperature (and in a wide temperature range) and therefore the possibility of operation under extreme conditions.

It is relevant to note that in ion-conducting PNLCCs considered here (consisting of NLC molecules included in polymers) the ion transport and the mechanism of ion-conductivity enhancement through dispersed NLC molecules is different from that in polymer–NLCs composites whose structure at microscopic and/or macroscopic levels is more complex, e.g., in PDLCs,⁶ where droplets (micro- or nanosized larger than 100 nm) of fluid NLCs are within the polymer matrix. At a relatively low concentration of the dispersed molecules of the NLCs confined in PEO, at room temperature and if their alignment is beforehand achieved (see Section 2.3), a local pathway for the ion migration in the former case may be the nanosurfaces of the aligned NLC molecules (those from them that are coupled to the polymer chains) or between them (Figure 8b). At a higher concentration of NLCs included in PNLCCs (but before the formation of distinct PDLC structures), very possible are various additional ion-conductive pathways induced by interfaces between the host polymer and formations of clustered NLC molecules (some of them coupled to the polymer chains—an irregular aggregation effect) (Figure 8c). Such an interfacial-transport variant of pathways has been discussed for ion-conducting PNLCCs, e.g., PVA/SCB/KI.¹² In

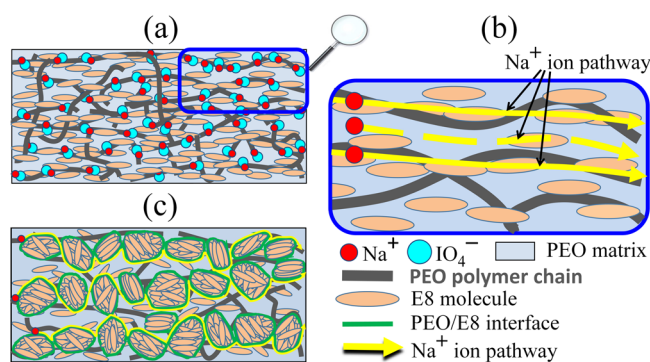


Figure 8. Schematic of possible pathways for Na^+ -ion conduction in the PEO/E8/ NaIO_4 system (unidirectional moving upon electric field applied) for (a, b) hypothetically aligned E8 NLC molecules dispersed in the PEO matrix (low weight fraction of E8); (c) clusters of E8 NLCs in the PEO matrix (at moderate weight fraction of E8 and no microdroplets of NLCs formed).

similar way, the phase boundary between separated phases in PDLCs (i.e., the region at the two-phase interface between the NLC microdroplet and its enveloping polymer surroundings) could be a pathway for ion migration. The effect depends on the characteristics of both the polymer and the NLCs, the spatial distribution of the two phases, the size of the NLC domains, temperature, and other factors. It has to be noted that if the NLC weight fraction is relatively high, e.g., above 30–40 wt %, the PNLCCs do transform into PDLC (or PDLC-like) structures containing phase-separated droplets of interacting NLC molecules forming a NLC mesophase. At a moderate concentration of NLCs in the PNLCCs, the structure of these composite materials can be considered as hybrid (continuous molecular and two-phase material), and the ion conductivity is governed by the polymer matrix rather than by the interface—the segmental motion of the polymer backbone is the most important determinant of efficient ion transport.

3.1.3. Thermal Behavior of Ionic Conductivity. Ionic conductivity is a strong function of temperature. From the impedimetric response of the ion-conducting PNLCCs, one can determine the temperature-dependent change in their ionic conductivity. This is illustrated in Figure 8 for PEO/E8 and PEO/E8/ NaIO_4 measured at temperatures below their glass-transition temperature (T_g) ($T_g = 52$ °C for PEO/E8 at compositional ratio w/w = 70/30% and $T_g = 42$ °C for PEO/E8/ NaIO_4 at compositional ratio PEO:E8: $\text{NaIO}_4 = 63:27:10$ wt %²⁰). One can find that at temperature $T < T_g$, σ of both PEO/E8 and PEO/E8/ NaIO_4 exponentially increases with the increasing T . The observed temperature-induced enhancement effect has been also established by studies on thin films of PNLCCs composed from linear-chain polymers, in which have been included NLCs whose molecular structure is similar to that of the compounds in the NLC E8, such as highly polar cyanobiphenyls.^{10,12,13,15}

The increasing trend in the $\sigma(T)$ behavior can be explained in terms of a thermally activated hopping transport model. The measured ionic conductivity as a function of reciprocal temperature presents the well-known phenomena (described by the Arrhenius equation: $\sigma \sim \exp(-E_a/kT)$) when an ionic conduction mechanism involves ion hopping, in accordance with the concepts for the electrical conduction mechanism for polymer-based ion electrolytes.²⁶ From the slope of the linear fit to the data in the example given in Figure 9c, one can determine

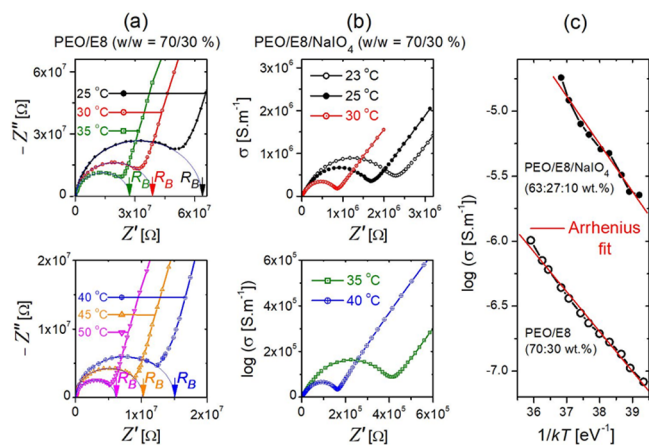


Figure 9. Nyquist complex impedance plots for 150 μm thin films of PEO/E8 (a) and PEO/E8/NaIO₄ (b) at various temperatures.²¹ (c) Arrhenius plots for the ionic conductivity of PEO/E8 and PEO/E8/NaIO₄—characteristics obtained in the temperature range below the glass-transition temperatures of these PNLCCs.

the value of the activation energy $E_a = 0.335$ eV for PEO/E8 and $E_a = 0.366$ eV for PEO/E8/NaIO₄. The three-dimensional Na⁺-ion diffusion pathways with such relatively low energy required for conduction provide the opportunity to achieve a high-rate capability of ion-conducting PNLCCs. As inferred from the measured thermal behaviors of ion conductivity of such ion–electrolyte systems,^{20,22} the NLCs are actively involved in ion transport and act as an ion-conducting pathway for electric charges (ions).

Significantly, the effect from NLCs included in PNLCCs is most pronounced when the temperature is slightly above T_g . In this case, an abrupt increase has been observed in the temperature dependence of ion conductivity, $\sigma(T)$.^{20,22} Still, in the temperature range $T_g < T < T_m$, where T_m is the melting temperature, the Arrhenius plots have a linear slope.²² This indicates that the ionic conduction occurs via a simple hopping mechanism. Such thermal behavior simply reflects the existence of crystalline and amorphous phases below T_g and only the amorphous phase close to T_m . The $\sigma(T)$ behavior of the considered ion-conducting PNLCCs is in accordance with the concepts for the electrical conduction mechanism in such media,²⁶ as well as in agreement with the dynamic bond percolation theory, the free-volume model of a glassy body, and the Vogel–Tamman–Fulcher equation that predict an enhancement of segmental motion and an increase in the free volume of the system at $T > T_g$.

3.1.4. Effect from the Crystalline Status. The NLCs-induced enhancement of the ion conductivity in PNLCCs is predominantly due to modification of their structural properties by the NLC additives. It has been well documented that if the concentration of the nematic included in the polymer is appropriate, then it can reduce the crystallinity of the polymer. The change of the crystalline status occurs during the synthesis of the PNLCCs due to interfacial interaction between the monomer and the NLC molecules in the polymerization process. The physical properties of polymers, and hence of ion-conducting PNLCCs, are strongly dependent on the degree of crystallinity (X_C).

X_C can be determined by X-ray diffraction (XRD) measurements. In the case of PEO/E8 composite considered here as an example, from XRD records (Figure 10 a) a reduction of X_C from 27% for neat PEO to 15% and 10% has been estimated,

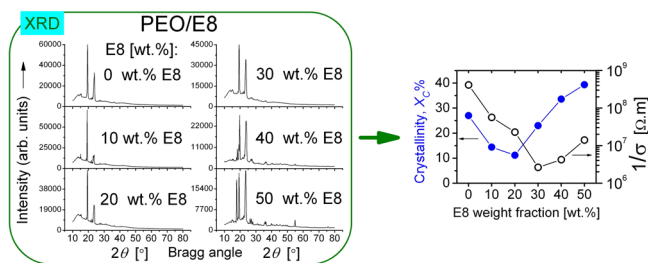


Figure 10. XRD pattern recorded for PEO/E8 PNLCCs at various weight fractions of the E8 NLCs. Right: the trend in the change of the degree of crystallinity ($X_C\%$) calculated from XRD data, as well as the reciprocal ion conductivity obtained by EIS measurements of PEO/E8 composites vs the weight fraction of the E8 NLCs (from work²⁴ under a Creative Commons License CC BY 3.0).

when the concentration of E8 NLCs is ca. 10 and 20 wt %, respectively²⁴ (Figure 10 b). Actually, NLCs in PNLCCs act as plasticizers increasing the amorphous phase in the host polymer, resulting in an enhancement of the polymer segmental motions. This favors the transport of free electric charges (ions) in the polymer-based ion-conducting systems (electrolytes) through the well-known mechanism of ion hopping via a flexible polymer network.²⁶ At a high weight fraction of NLCs in PNLCCs, e.g., above 30 wt % in PEO/E8, the amorphous region should be increased. Also, the formation of the massive phase-separated structure of closely located large microdroplets (20–30 μm diameter) of bulk NLCs encapsulated within the PEO polymer matrix¹⁶ destroys the polymer order and lowers the polymer crystallinity. In this case, however, the opposite trend was observed—the crystallinity index X_C increases (Figure 10 b). This paradox is related to the increased numbers of intermolecular structures formed from NLC molecules and the host polymer at higher NLC concentration, an effect that is reflected in the XRD patterns clearly showing the growth of an additional sharp peak of diffraction^{22,24} (Figure 10 a).

In particular, the interrelation between X_C and the reciprocal ion conductivity of PEO/E8 composite material can be seen in Figure 10b. The enhancement of the amorphous phase in PNLCCs by the NLC additives is the main reason for the acceleration of the mobility of the free ions and increase in the ionic conductivity on PNLCCs. In general, the considered enhancement effect in the LC–polymer composites due to interfacial interaction between the polymer and the dispersed LC molecules is predetermined by the chemical structure of the LC, the LC mesophase, and characteristics (e.g., the anchoring) of both interfaces (LC and polymer). The same applies to ion-conducting PNLCCs having ion donors, e.g., metal–ion salt-complexed PNLCCs. In this case, the addition of the salt to PNLCCs can lead to a further increase in the percentage of the amorphous portion, and this effect may be considerable.^{17,22}

3.2. Dielectric Properties of Ion-Conducting PNLCCs. Studies of the dielectric behaviors of the ion-conducting PNLCCs provide important information necessary for the applications of these dielectrics.

3.2.1. Dielectric Permittivity. The complex dielectric permittivity function ($\epsilon^* = \epsilon' - i\epsilon''$) provides detailed information about the polarization and dielectric relaxation. In the case when the dielectric material is in a plane-parallel capacitor geometry in an AC electric field, the real and imaginary parts of ϵ^* , i.e., the storage component ϵ' and the loss component ϵ'' , can be calculated from data measured for the complex electrical impedances, by using the following relations:

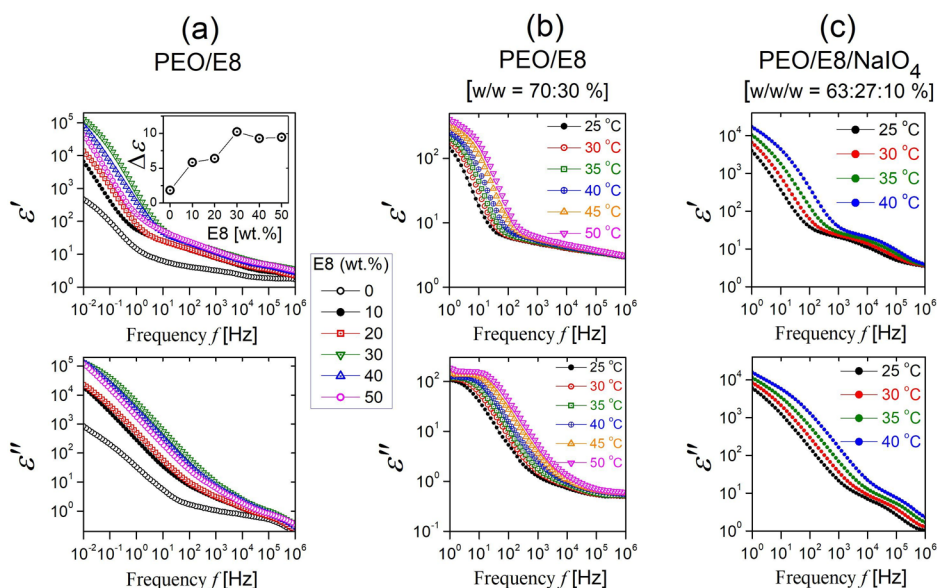


Figure 11. (a) Frequency spectra of real (ϵ') and imaginary (ϵ'') parts of complex dielectric permittivity obtained for 150 μm thin films of PEO/E8 at a different concentration of E8 NLCs (inset: plot of the dielectric strength $\Delta\epsilon$ vs the E8 weight fraction). $\epsilon'(f)$ and $\epsilon''(f)$ spectra for PEO/E8 (b) and PEO/E8/NaIO₄ (c) at various temperatures.

$\epsilon' = -Z''d/2\pi f\epsilon_0AZ|Z|^2$ and $\epsilon'' = Z'd/2\pi f\epsilon_0AZ|Z|^2$ where ϵ_0 is the vacuum permittivity and d and A are the thickness and the electrically active area of the sample, respectively. As for the electrical conductivity, the dielectric properties of ion-conducting PNLCCs are governed by their two components, the polymer and the NLCs. Depending on the amount of NLC fraction, dielectric materials with modified permittivity can be produced. As with the ion conductivity, the possible electrostatic interaction between polar molecules of NLCs and certain functional groups in the polymer chains can affect the dielectric properties of PNLCCs. The dielectric permittivity of ion-conducting PNLCCs can be enhanced as compared to that of the host polymer. Various factors may play a role in this. In the case of the PEO/E8 composite (Figure 11 a), the enhancement effect is a result from interactions between PEO oxygen and the polar NLC molecules of E8 dispersed in PEO.²²

As an indicator of the dielectric enhancement due to the inclusion of NLCs in the polymer host, one can use the value of the dielectric strength $\Delta\epsilon = \epsilon'_s - \epsilon'_\infty$ of the PNLCC dielectrics; ϵ'_s and ϵ'_∞ are the values corresponding to the static and high-frequency limit of ϵ' , respectively, obtained from experimental ϵ' spectra. The quantity $\Delta\epsilon$ is a measure of the dipole polarization. In the case shown in Figure 11a, $\Delta\epsilon$ is calculated as $\Delta\epsilon = \epsilon'(1 \text{ kHz}) - \epsilon'(1 \text{ MHz})$ according to the specifics of the ϵ' spectral data. The plot of $\Delta\epsilon$ against the NLC content shows that the dispersion of NLCs E8 in the polymer PEO leads to enhanced dielectric properties of the composite dielectric material PEO/E8. The increasing $\Delta\epsilon$ implies an increase of polarization, a presence of molecular dipoles, a dipole contribution to the polarization, and an enhanced electro-dipolar character of PNLCCs.²⁰ Reasonably, the change in the dipolar character (and dipole–dipole interaction) of PNLCCs depends on their composition. Significantly, the behavior of $\Delta\epsilon$ resembles the effect of the ion conduction enhancement by varying the NLC content in the PNLCC (recall Figure 7 c). This suggests that both effects are controlled with the same mechanism. Enhancement of the dielectric properties induced from the included

NLCs has also been reported for other PNLCCs, e.g., PVDF/SCB.⁹

As for ion-doped PNLCCs, for example, salt-complexed polymer electrolyte systems such as PEO/E8/NaIO₄, their dielectric properties may be strongly affected by structural modification induced from the ionic dopant.^{17,20} This is due to the interaction of the ion-donating compound with the polymer molecules (forming coordination complexes) and the increase in the free volume in the amorphous region of the PNLCCs.²⁰ As compared to the corresponding undoped PNLCCs, the ion-doped PNLCCs exhibit an enhanced dielectric response (in particular, this can be seen by comparing Figure 11b and Figure 11c).

Using the methods of dielectric spectroscopy, the analyses of the dielectric permittivity function upon temperature variation (Figure 11 b and c), as well as the temperature dependencies of the dielectric loss tangent, AC conductivity, and molecular dynamics, namely, the dielectric relaxation of ion-conducting PNLCCs, revealed that the improvement of the dielectric properties of these ion conductors is mainly due to the increase of the amorphous portion in the host ion-conducting polymer as a result of the included NLCs.²⁰

The dielectric properties of materials can be expressed in terms of the complex permittivity as Cole–Cole plots, i.e., the graphs of ϵ'' vs ϵ' , with frequency f as a parameter. Figure 12a presents the Cole–Cole plots of the PEO/E8 composite. As is known, the Cole–Cole model can describe the secondary relaxations in the dielectric materials. The Cole–Cole presentation is useful for the interpretation of molecular dynamics of dielectrics which possess one or more well-separated relaxation processes. The relaxation frequency (f_R) of the polarization can be extracted from the relaxation behavior of the material by fitting the experimental data of dielectric spectra with the Cole–Cole approach of the Debye equation: $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon'_\infty + \Delta\epsilon[1 + (i\omega\tau)^{1-\alpha}]$, where $\omega = 2\pi f$ is the angular frequency, $\Delta\epsilon$ is the dielectric strength of the material, τ is the relaxation time, and α is the distribution parameter that ranges from 0 (infinitely broad distribution) to 1 (Debye's single

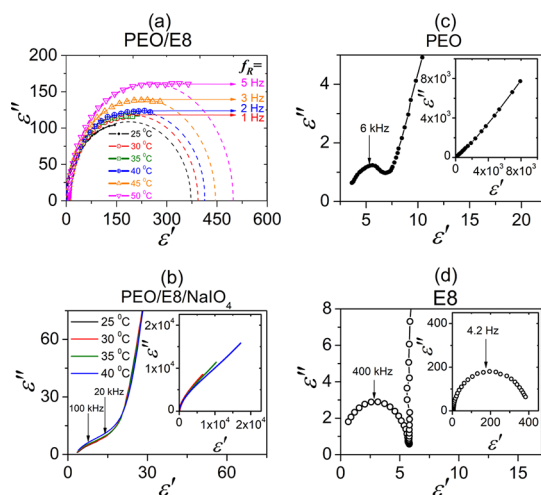


Figure 12. Cole–Cole plots for 150 μm thin films of PEO/E8 (w/w = 70/30%) (a) and PEO/E8/NaIO₄ (w/w/w = 63/27/10%) (b) at various temperatures. The semicircle approximating the shape of each (ϵ'' vs ϵ') curve in (a) is the fit performed for the data and represents a Debye relaxation process of dipole polarization. The frequencies f_R that correspond to the maximum of ϵ'' for each semicircle are denoted. For the sake of comparison, Cole–Cole curves for a 150 μm thin film of PEO (c) and 25 μm thin film of E8 NLC (d) are also given. Insets: the Cole–Cole plots in a full range.

relaxation time limit). When $\alpha = 0$, the Cole–Cole model is reduced to the Debye model.

The complex Cole–Cole diagrams can be fitted to form semicircles. In this case (illustrated in Figure 12 a), the frequency (f_R) corresponding to the apex of the Cole–Cole semicircle is an intrinsic characteristic of the dielectric material and is associated with the relaxation relevant to the ionic contribution to the dielectric relaxation process. At that frequency and for the relaxation time $\tau_R = 1/f_R$, the dielectric heating is maximum, and the dissipation factor is also maximum. That is why the value of this frequency is also one of the important characteristics of the dielectric relaxation properties of the materials.

In particular, Cole–Cole plots in Figure 12a indicate that the PEO/E8 ion-conducting PNLCC is characterized with a low value of the frequency f_R (a few Hz). Further, f_R increases as the temperature increases. The observed change of f_R is closely related to the ion conductivity (σ) of the dielectric material. The quantity σ also increases with the increasing temperature (recall Figure 9). The shift of f_R toward the higher frequencies implies an increase in the diffusion mobility of free ions with elevating temperature. This is reasonable taking into account the thermally enhanced flexibility of the polymer chains in the considered plastic dielectric materials.²²

Cole–Cole plots for salt-complexed PEO/E8/NaIO₄ exhibit no distinctive shape (Figure 9 b). This is due to the high ion conductivity of this PNLCC. The departure from the semicircle is significant in the low-frequency part of Cole–Cole plots. In the high-frequency part of the complex permittivity diagram, a semicircle-like feature can still be observed in the region at about 20–100 kHz. By contrast, the shapes of Cole–Cole plots for the PEO polymer (Figure 12 c) and E8 NLC (Figure 12 d) are simple in form.

3.2.2. Electric Modulus. Because of the relatively high electrical conductivity of PNLCCs, their dielectric characterization should be performed in terms of the complex (di)electric

modulus (M^*). M^* is one of the principal dielectric functions used to obtain information on the dielectric materials. By the electric modulus formalism, one can overcome the limitation imposed by the electrode interfacial polarization at low frequency, and thereby the relaxation processes can be more clearly observed. Electrical relaxation phenomena in ion-conducting polymer-based dielectrics, such as PEO/E8 and PEO/E8/NaIO₄ exemplified here, are known to be caused from phase transitions, interfacial effects, and polarization or conductivity mechanisms. The complex impedance (Z^*) data can be transformed into the complex electric modulus (M^*) by the expression $M^* = M' + iM'' = 1/\epsilon^*$, where the real (M') and imaginary (M'') parts of M^* are defined through the real (ϵ') and imaginary (ϵ'') parts of ϵ^* by the expressions $M' = \epsilon' / [(\epsilon')^2 + (\epsilon'')^2]$ and $M'' = \epsilon'' / [(\epsilon')^2 + (\epsilon'')^2]$, respectively.

In the M^* representation, a relaxation peak observed in the frequency spectra of M'' is indicative of the conduction process. Figure 13a displays the frequency-dependent values of M' and

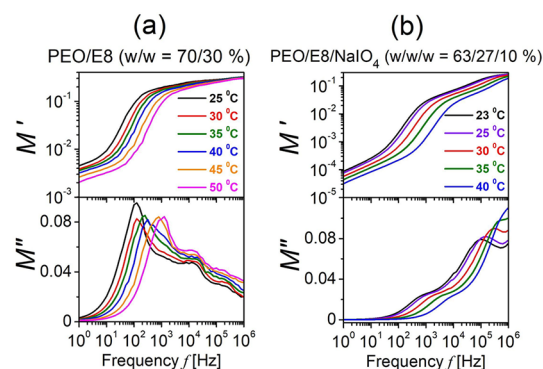


Figure 13. Frequency spectra of the complex electric modulus calculated for 150 μm thin films of PEO/E8 (a) and PEO/E8/NaIO₄ (b) at various temperatures.

M'' calculated for the case of PEO/E8 film at various temperatures. In the low-frequency region, both M' and M'' approach zero. Their very low values are due to the electrode polarization effect. The tails seen in the low-frequency side of the M' spectra, followed by a rapid increase of M' and M'' values toward higher frequencies, result from the capacitance associated with the dielectric properties of the sample. In the high-frequency range, M' tends to saturate. The $M''(f)$ spectra exhibit a relaxation peak that is centered at the dispersion region of $M'(f)$ (Figure 13 a). This peak indicates that the sample is an ion conductor and is associated with dielectric-relevant conductivity relaxation at the corresponding frequency $f_{DR(M'')}$. The presence of a distinct peak in the M'' dispersion implies that ionic motions and polymer segmental motions are strongly coupled. From that, the increase of the M'' value by increasing f on the low-frequency side of the peak ($f < f_{DR(M'')}$) is relevant to random hopping of mobile charge carriers over a long distance (in our case, they are ions originating mostly from PEO, since the ions from E8 are less). On the high-frequency side of the relaxation peak present in the $M''(f)$ spectra (i.e., at $f > f_{DR(M'')}$), the long-range motion of ions is restricted—the polymer segmental motion is less favorable for the ion transport, and the ionic motions occur in shorter ranges.

The shift of the relaxation peak in $M''(f)$ spectra toward higher frequencies at elevated temperatures (Figure 13 a) is associated with a faster relaxation of the active ions at higher temperatures. Such a trend is usually reported for ion-

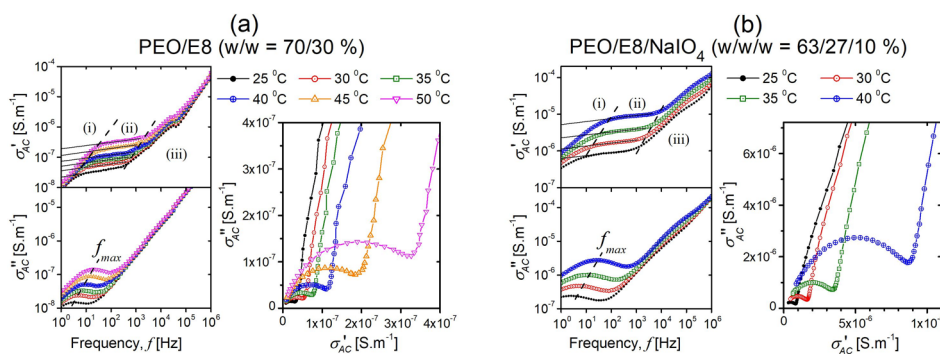


Figure 14. Frequency dependence of the real (σ'_{AC}) and imaginary (σ''_{AC}) parts of AC conductivity, as well as the plot σ''_{AC} vs σ'_{AC} for 150 μm thin films of PEO/E8 (a) and PEO/E8/NaIO₄ (b) at various temperatures.²¹

conducting polymer-based systems at increasing temperatures.²⁷ The increase in the value of $f_{DR(M'')}$ is related to the increase in ionic mobility and the increase of ionic conductivity. For PEO/E8 and PEO/E8/NaIO₄, the increase of ionic mobility and ionic conductivity with temperature in the range below the glass-transition temperature has been established in the works of Koduru et al.^{16,17} The conductivity relaxation near 100 Hz at room temperature means that the hopping of charge carriers in PEO/E8 PNLC is relatively slow. Nevertheless, this ionic conductor possesses valuable electrical properties, specific behaviors at low frequencies,³⁴ and other useful features, arising from the NLCs, that make it an interesting material for electrical engineering, organic electronics, mechatronics, and sensorics.

The frequency-dependent behaviors of the electric modulus of ion-doped PNLCs can differ from those of the corresponding base (undoped) PNLCs. Notably, the inclusion of an ion donor in PNLCs leads to a large shift of the relaxation frequency $f_{DR(M'')}$. For instance, Figure 13b depicts the electric modulus frequency spectra obtained for PEO/E8/NaIO₄. In this case, the peak present in the high-frequency side of the $M''(f)$ spectra reflects a relaxation mechanism—dielectric-relevant conductivity relaxation. The large spread around the peak in the $M''(f)$ spectra indicates the dominance of non-Debye type relaxation behavior in the PEO/E8/NaIO₄ ion-electrolytic system. Like for PEO/E8, the shift of this peak toward higher frequencies with increasing temperature (but in the range below the glass-transition temperature) is relevant to the increase in ionic mobility and the increase of ionic conductivity of PEO/E8/NaIO₄ ion-conducting PNLC with the temperature^{17,22} (recall Figure 9). These effects in ion-conducting PNLCs originate from the enhanced polymer segmental motion upon increasing temperature.²⁷ The conductivity relaxation in ion-doped PNLCs occurs at high frequency (~ 100 kHz at room temperature, in the example for PEO/E8/NaIO₄ in Figure 13b). This means that the ion-doped ion-conductive PNLCs enable a very fast ion migration (a fast hopping of charge carriers)—an electrical property that is advantageous for soft-electronics applications.

3.2.3. AC Conductivity. The frequency-dependent (AC) complex electrical conductivity (σ^*_{AC}) is also one of the key physical characteristics of ion-conducting PNLCs. The real part (σ'_{AC}) and imaginary part (σ''_{AC}) of AC conductivity $\sigma_{AC} = \sigma'_{AC} + i\sigma''_{AC}$ are defined by $\sigma'_{AC} = 2\pi f\epsilon_0\epsilon''$ and $\sigma''_{AC} = 2\pi f\epsilon_0\epsilon'$. The variation of σ'_{AC} and σ''_{AC} as a function of the frequency f of the applied electric field is indicative of the mechanism of the ion transport and is a further representation of the dielectric phenomena. The $\sigma'_{AC}(f)$ and $\sigma''_{AC}(f)$ behaviors of ion-

conducting PNLCs can be illustrated with data obtained for thin films of PEO/E8 and PEO/E8/NaIO₄ (Figure 14). At increasing temperature, both quantities σ'_{AC} and σ''_{AC} show an increasing trend, well pronounced in the middle- and low-frequency range, respectively.

As is known, σ'_{AC} is related to the dissipation of electrical charges and represents the dissipation of energy due to the flow of charge carriers (i.e., flow of energy). The $\sigma'_{AC}(f)$ behaviors shown in Figure 14 can be described by the Jonscher's power-law model, giving the link between AC conductivity and charge carrier motion: $\sigma'_{AC}(\omega) = \sigma_{dc} + C\omega^n$, where $\omega = 2\pi f$ is the angular frequency, C is a temperature-dependent pre-exponential constant, the power factor n should fall in the range from 0 to 1, and σ_{dc} denotes the frequency-independent conductivity (the so-called “static”, direct current (DC) electrical conductivity), i.e., the value of $\sigma''_{AC}(\omega)$ at $\omega \rightarrow 0$. Since the Jonscher's power law represents the charge transport mechanism and many-body interactions among charge carriers, from the $\sigma'_{AC}(f)$ behaviors one can obtain physical information about the role of the accumulated interfacial charges and permanent/induced polarization for the increase of conductivity as the frequency of the applied AC electric field increases.

In the examples shown in Figure 14a and b, the plots $\sigma'_{AC}(f)$ in double logarithmic scales exhibit three separated regions with linear slopes, typical for disordered semiconductors: (i) low-frequency region corresponding to dominance of electrode polarization, (ii) middle-frequency region associated with DC conductivity, and (iii) high-frequency dispersion region, respectively. The temperature-dependent values of σ_{dc} can be extracted from the intermediate region of $\sigma'_{AC}(f)$ according to the Jonscher's power law. Reasonably, the $\sigma_{dc}(T)$ dependence obtained in this way should resemble that for $\sigma(T)$ obtained directly from EIS data (in Figure 9).

The local maximum (at the particular frequency value termed f_{max}) seen in the $\sigma''_{AC}(f)$ plot at each temperature corresponds to the buildup of polarization. At this frequency, complete buildup of the polarization process occurs. It is seen from Figure 14a and b that f_{max} increases as the temperature increases. The shift of f_{max} toward higher frequency indicates an increasing number of charge carriers (ions) for migration.²¹ The plots of $\sigma''_{AC}(f)$ against $\sigma'_{AC}(f)$ at a given temperature in the range below the glass-transition temperature exhibit semicircles followed with a spike/tail. By “sigma representation”, the diameter of the semicircle is reciprocally (inversely) proportional to the relaxation time (τ). At increasing temperature, the diameter of the semicircle increases (Figure 14a and b); i.e., τ becomes lower—the ion migration occurs faster. The same

trend obtained from complex AC conductivity analyses has been reported for various polymer-based ion-conducting dipolar systems.³⁵ The cause for the decrease of the relaxation time is the same as for the increase in ionic conductivity, namely, the increase of molecular chain segmental dynamics with increasing temperature.^{21,22}

4. PREPARATION OF ION-CONDUCTING PNLCCS

The most common and simple technique for the preparation of stable PNLCCs is the conventional solution casting. By this process, in order to include and disperse the NLC molecules into the polymer, a solution of monomers is mixed with a solution of NLCs to form a homogeneous mixture, which is then poured into a polymer film. A solution of ion-donor compound can also be added to synthesize ion-conducting PNLCCs. By the solution cast technique, the preparation of homogeneous thin composite films can be well controlled by the solvent evaporation rate. In this way, stable free-standing thin films with high flexibility and a thickness of 100–200 μm can be formed relatively easy, possessing desirable mechanical, conductive, dielectric, thermal, and other properties.^{10–13,15–17,22} As an example, Figure 15 illustrates the

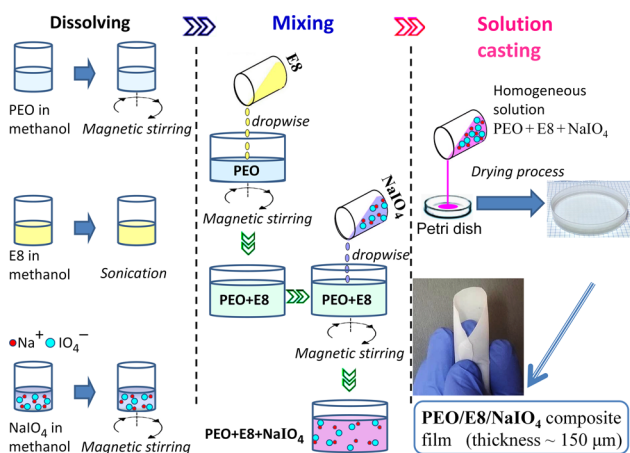


Figure 15. Schematic representation of the fabrication steps of PEO/E8/NaIO₄ ion-conducting PNLCC (by means of the solution cast technique).

preparation of PEO/E8-based ion-conducting PNLCCs (following the works of Koduru et al.).^{16,17} Also, highly stretchable conductive materials based on PNLCCs can be manufactured following the well-developed PDLC technology.⁷

The organic polymers suitable for the production of high-performance ion-conducting PNLCCs must satisfy numerous properties simultaneously—they should be ion-conducting, with good chain flexibility, sufficient electrochemical stability, low electronic conductivity, excellent mechanical properties, thermal stability in a wide range of working temperatures, strong solvating ability for the mostly used metal ions, high dielectric constant, and other specific properties and necessary characteristics. Moreover, the polymer hosts should possess several essential characteristic features such as polarity and effective electron-donating ability to form coordination bonds with cations. Aiming at biomedical applications, highly desirable is the polymers' biocompatibility. Importantly, the features of easy fabrication, low cost, and high safety are also good reasons for the polymer choice. Some of the most employed plastic polymers for the fabrication of ion-conducting PNLCCs have

been the following: poly(ethylene oxide) (PEO),^{16,17,22} poly(vinyl alcohol) (PVA),^{11–13} poly(vinylidene fluoride) (PVDF),⁹ poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP),¹⁵ and polyacrylonitrile (PAN).¹⁰

The NLCs included in PNLCCs should also possess suitable properties, such as molecular polarity and excellent chemical and thermal stability over a wide temperature range (preferably at ambient temperatures). In particular, NLCs from the cyanophenyl family are very attractive for the development of ion-conducting PNLCCs.^{9,11–13,15} In many studies and applications, commercial multicomponent NLC mixtures like the well-known E7 and E8, consisting of such cyanophenyl NLC compounds, have been used.^{10,16,17,22} The successful synthesis of ion-conducting PNLCCs must be accompanied by achieving a homogeneous dispersion of NLCs into the polymer host, thus obtaining uniform PNLCC materials with a good quality.

Various ionic compounds can be employed as ion donors in ion-conducting PNLCCs. In particular, following the well-developed technology for solid polymer electrolytes for rechargeable batteries, very appropriate are some ionic salts of alkali or alkaline-earth metals, of which those that are preferable are environmentally friendly, nontoxic, low cost, and earth abundant. It should be mentioned that for ion-doped PNLCCs, their composition has to be carefully chosen because a reduction of the ion conductivity is rather possible at higher concentrations of the ion donors. For example, in the case of PEO/E8/NaIO₄ salt-complexed PNLCCs considered here, the increase of the concentration of the salt NaIO₄ up to 10 wt % leads to a decrease in their crystallinity and an enhanced Na⁺-ion conductivity (at a fixed PEO:E8 wt % ratio). Thus, at 10 wt % salt, the composite PEO/E8/NaIO₄ exhibits a 15% lower degree of crystallinity and a 20 times higher ion conductivity than PEO/E8.¹⁷ However, further increase of the salt concentration up to 15 wt % (at the same PEO:E8 wt % ratio) resulted in a drop of Na⁺-ion conductivity by a factor of 50, as well as in a 20% increase in the degree of crystallinity as compared to PEO/E8.¹⁷

Regarding the optimal concentration of NLCs in the polymer ionic electrolytes with an ion donor, this must also be very carefully considered in order to produce high-performance highly conductive PNLCCs having the desired electrochemical and thermal stability. Through their function as plasticizers, the NLCs do increase the ionic conductivity of PNLCCs by suppressing the crystallinity of the polymer and increasing the flexibility of the polymeric backbone. Moreover, the molecules of the NLCs can promote additional pathways for enhancement of ion conductivity; i.e., the NLCs can provide the second route for the ion transport (the first one is via the polymer network). However, the possible electrostatic interaction and the resulting coupling of NLCs with the polymer chains may compete with the effect from the inclusion of the ion-donor compound (e.g., the salt–polymer complexation); thus, the ionic conductivity of PNLCCs may become limited when the concentration of their NLC constituent becomes too high.²²

As a good practice, most of the works on ion-conducting PNLCCs have been concentrated on the optimization of their ion-conducting, dielectric, mechanical, and other properties, on the basis of the characteristics experimentally obtained by inspection of various compositions of these materials.^{9,10,12,13,16,17,22} For that, very useful are the thorough studies of key properties and characteristics of ion-conducting PNLCCs produced by use of nematics that are members of homologous series, e.g., in the work of Kamarudin et al.¹⁵ Thus, one can

optimize the morphology, conductivity, and dielectric and electrochemical properties of PNLCCs, as well as the performance of the devices fabricated thereof. This will be beneficial for future ionic device applications based on ion-conducting PNLCCs.

The selection of ion donor is paramount to the improvement of these ion conductors. There are many successful combinations of ions together with a chosen ion-conducting polymer and dispersed NLCs. The conductive ion species can lead to a significant change in the physicochemical properties of ion-conducting PNLCCs, thereby reflecting on their application feasibility. An important reason for choosing metal cations of small radius (Li^+ , Na^+ , K^+ , etc.) is their ability to be coordinated with the chain segments of the host polymer. In particular, Na^+ -based salts are found to give an excellent overall performance in terms of conductivity and stability.¹⁷ Furthermore, the use of Na ionic compounds can be an alternative to lithium-based salts (known to affect the environment).

The design and preparation of novel ion-conducting PNLCCs, as well as the development of novel techniques of their fabrication and device construction, are challenging tasks. Surely, one of the main challenges is to invent a way to increase the orientation order of the NLCs within the PNLCCs. Another very important task is the increase of the effectiveness of ion-conducting PNLCCs toward specific applications such as chemical sensing and medicine. Also, the production of novel PNLCC electrolyte materials with microscopic porosity is welcome, since they are attractive for fundamental research and industrial applications.

In the past few years, the research works have made significant progress in developing new flexible thin-film composite materials engineered from polymers and NLC molecules, improving performance, and expanding their application field. Very recently, in 2022, effective strategies were proposed for this purpose. For instance, Liu et al.⁹ reported on a synergistic improvement in dielectric constant and energy storage properties of PNLCCs due to intermolecular interaction between the NLCs SCB and polymer poly(vinylidene fluoride) (PVDF) in flexible PVDF/SCB composite films. Zeng et al.¹⁸ provided an interesting approach for fabrication of electrolytic material constructed as a semi-interpenetrating network of novel nematogen liquid crystals (C6M) and the polymer poly(ethylene glycol) diglycidyl ether (PEGDE), for flexible lithium–metal batteries. The NLCs in this synthesized polymer electrolyte create stable and efficient ion transport channels. Such design of an ion-conducting network resulted in improvement of both the ion conductivity and the mechanical flexibility of the produced ion electrolyte membranes. Currently, the development of high-performance PNLCC ionic electrolytes for practical applications remains a vast area for innovation and rationalization.

5. APPLICATIONS OF ION-CONDUCTING PNLCCS

The electrical conductivity, dielectric, mechanical, film-forming, and other significant properties of the ion-conducting PNLCCs are an attractive premise for various practical applications, mostly in the fields of electronics and ionics, energy, and sensing (Figure 16). The potential applications of such multifunctional materials have been increasing significantly, including nowadays areas such as mechatronics and engineering of flexible ionic and flexoionic devices with various functionality, highly responsive to distinct stimuli, and well controllable.

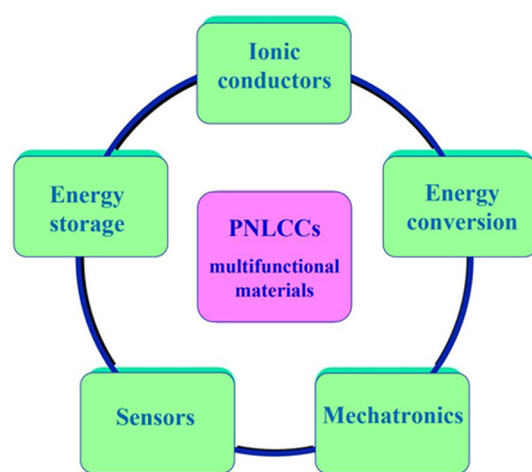


Figure 16. Major application areas of PNLCCs.

The main application of these advanced materials is for the production of polymer electrolytes in energy devices, especially for flexible rechargeable mini-batteries and capacitors for flexible and portable electronics, and for use in stretchable, wearing, and printed electronics. Clearly, these high-tech applications motivate researchers and industry experts to increase their activity toward synthesis of novel ion-conducting PNLCCs with enhanced properties, to explore them, and to devise novel concepts for the design of such complex electrolyte materials.

Essentially, the results obtained for the conductivity of PNLCCs that is of paramount importance for the most explored areas of their application^{10–13,15–17,20,22} indicate that these ion conductors are suitable for thin-film applications in organic electronics and sensorics, as well as in mechatronics, utilizing also their dielectric properties as well as their flexoresponse to electromagnetic fields. In some cases, the applications of ion-conducting PNLCCs may be similar to those of the PDLCs and composites from polymers and ionic liquids (for thorough reviews, one can refer to Zhang et al.⁶ and Correia et al.,²⁹ respectively).

Regarding the ion-conduction performance of PNLCCs, it should be noted that the NLC molecules dispersed in PNLCCs can lead to an enhancement effect that may be comparable to that achieved by ion-transporter polymers blended with a suitable highly amorphous polymer. The latter is purposely employed in order to suppress the crystallinity of the ion-transporter polymer and thereby to improve its electrolytic properties. For instance, the comparison of room-temperature ionic conductivities of PEO/E8/NaIO₄ and PEO/PVP/NaIO₄ composite polymer electrolyte systems that have an equal compositional ratio (w/w/w weight fractions, in wt %) can be pointed out.²² The amorphous polymer poly(vinylpyrrolidone) (PVP) is often used as a partner of PEO in polymer–ion electrolyte systems. As is known, this polymer breaks the regular arrangement of PEO and the amorphous region is expanded, resulting in a significant decrease in crystallinity. Importantly, the carbonyl group (C=O) in PVP enables formation of different complexes of alkali-metal ion salts at a wide range of concentrations. Although the supporting and enhancing mechanisms for the transport of Na⁺ ions are different in PEO/E8/NaIO₄ and PEO/PVP/NaIO₄ ion–polymer systems,²² the mechanism for Na⁺ ion conduction in both electrolytes is the same—a hopping through the structural units of PEO. Significantly, the very close values of ion

conductivity of the two compared electrolytes, PEO/E8/NaIO₄ and PEO/PVP/NaIO₄, at equal concentrations of the ionic salt NaIO₄ demonstrated the feasibility of the concept of ion-conducting PNLCCs. Respectively, these ionic conductors can be employed just like the polymer-blend electrolytes according to the purpose of the application.

Further, due to the possibility of forming flexible electrolyte membranes with enhanced response and functionality,^{12,18} the ion-conductive composites of specific polymers and NLCs are extremely interesting for production of flexible plastic electrochemical sensors and biosensors and for biomedical diagnostics and monitoring in membrane systems. For such applications, some of the functionalities of the composites may result from the intrinsic properties of the NLCs, and other responses may be due to the analytes-induced interaction of the NLCs with polymers. In any case, the chemical structure of the NLCs in the PNLCCs must meet the specific requirements of the given application. Possessing high plasticity and flexibility, PNLCC films can be made into any desired shape according to the requirements. As with polymer–NLCs composites with distinctly separated phases (PDLCs), the NLCs can improve the mechanical properties of the composites from polymers and molecular NLC materials, following the reduction in crystallinity of the polymer host. This applies to both blendlike structures and semi-interpenetrating network architectures. In the latter case, remarkable mechanical strength and flexibility due to formation of dense network structures in PNLCC plastic films have been reported. For example, stress–strain plots of flexible 195 μm thick electrolyte membranes prepared from specially synthesized C6M nematogen LCs, the polymer PEGDE, and the salt LiTFSI as a donor of working ions have demonstrated a tensile strength of 0.59 and 0.16 MPa for compositions of C6M/PEGDE/LiTFSI [w/w/w] = 23.3/46.6/30 and 46.6/23.3/30, respectively.¹⁸

Notably, the spectrum of the applications of ion-conducting PNLCCs is narrower than that of the composites of polymers and ionic liquids, and their derivatives and modifications having diverse and chemical structures that can include various organic cations and organic or inorganic anions thus can perfectly meet the requirements of the specific sensing applications.²⁹ For ion-conducting PNLCC thin films, after proper chemical treatment or/and functionalization of their surfaces, stable, reliable, portable, and flexible thin-film sensors can be constructed to electrically detect different substances exploiting certain interfacial molecular events. This is an innovative area that is yet to be developed.

In particular, the electrically based detection and sensing by the polar NLC molecules in ion-conducting PNLCCs can be realized through porous (macroporous) membranes of such organic materials and by using the response of certain functional groups of the included NLCs. In this way, membranes of ion-conducting PNLCCs can be chemosensitive to adsorption of organic compounds of chemical, biochemical, medical, or ecological interest. Moreover, these membranes could be specially patterned. Thus, ion-conductive PNLCCs may find emerging microanalytical applications utilizing the advantages of ion-conducting polymers, porous materials, and NLCs with their high polarity. For that, a selective adhesion of the analytes at the interface and/or into the microvoids structure of ion-conducting PNLCC membranes can be electrically detected by registration of the change in their conductivity (resistivity) or dielectric characteristics.

Another very important application field of ion-conducting PNLCCs is organic photovoltaics. Their use as polymeric electrolyte components in solar cells is well-known. Such advanced application in dye-sensitized solar cells (DSSCs) has been first reported by Kim et al. in 2009.¹⁰ This invention differs substantially from the efforts to integrate PDLCs with solar cells.³⁶ Further research in the field of solar cells revealed the potential of this innovation approach. In particular, in the study of Kamarudin and co-workers,¹⁵ ion-conducting PNLCCs have been fabricated using the poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) and cyanobiphenyl-based NLCs. For a series of such composites synthesized with NLCs having different alkyl chain lengths (5CB, 6CB, 7CB, 9CB, and 10CB, as members of the 4-*n*-alkyl-4'-cyanobiphenyl homologous series), the authors have found that the shorter alkyl chain NLCs have a better performance in terms of ionic conductivities and power conversion efficiencies of the fabricated photovoltaic devices.

The ion-conducting PNLCCs have interesting dielectric properties. Accordingly, such dielectric materials have been used for manufacturing of energy-storage devices, which have gained much attention in recent years. A recent example is the work on development of composites from NLCs 5CB and polymer PVDF by Liu et al.⁹ The authors have demonstrated that the 5CB organic filler with high polarity can be perfectly mixed and interact well with PVDF, thus forming dense and high-quality dielectric polymer films. This approach enables the production of thin dielectric films of 5CB/PVDF composite that exhibit a high dielectric constant of 9.8 (at 1 kHz and room temperature) and a high discharge energy density of 11.7 J cm⁻³. In this way one can enhance the energy storage capacity of dielectric film capacitors for their miniaturization and integration into lightweight electronic devices. Importantly, by the simple and inexpensive synthesis method proposed from Liu and co-workers,⁹ one can prepare various high-performance flexible dielectric devices based on PNLCCs. This area of energy devices based on ion-conducting PNLCCs has a great potential for further development. Clearly, more research is needed that could efficiently refine and expand their applications in dielectric devices.

In most applications, the PNLCC films with a thickness typically 100 to several hundred micrometers are intended to be used primarily at room temperature and at relatively low operating voltages (as low as possible). However, for high-voltage and high-power practical applications (such as energy storage devices, dielectric film capacitors, thin films in high-speed digital circuitry, microelectronic components, and pulse-power systems), the resistance of such composite materials against electric field-induced breakdown (the dielectric breakdown strength, E_{DBS}) is significant, especially at small thickness of the PNLCC films. Unfortunately, no data for E_{DBS} can be found in the literature for PNLCCs considered here (such information is available for other types of polymer–NLCs composites, such as electrically controlled PDLCs, that are however not the focus of the present mini-review). Most probably, the presence of NLCs leads to reduced values of E_{DBS} for the PNLCCs compared to that of PEO itself (typically $E_{DBS} \sim 50\text{--}60$ V/μm for PEO, e.g.,³⁷) depending on molecular weight and other factors). In particular, experiments with AC (at 200 Hz) and DC electric field transversally applied to 100 μm thin films of PEO/E8 and PEO/E8/NaIO₄ PNLCCs (at room temperature, no mechanical stress, stainless steel flat electrodes

with a minimal roughness) have shown no electric field-induced breakdown using field intensity of up to 5 V/ μm .

6. CONCLUDING REMARKS

The ion-conducting composites produced from polymers and nematic liquid crystals (PNLCCs) are multifunctional materials of current interest. These ionic conductors combine the advantages of the polymer ionic electrolytes with the ion-conducting and dielectric properties, the flexibility, and functionalities of the polar NLC molecules included in plastic materials. Having suitable mechanical, electrical, dielectric, thermal, and other properties, as well as relatively easy preparation, chemical stability, and excellent film-forming properties, and providing high mobility of charge carriers, such all-organic soft-solid composite materials have outstanding potential for advanced applications.

In recent years, research works have made significant progress in developing ion-conducting PNLCCs with improved properties and expanding their application fields. The research efforts contribute to the quality and performance of these ion conductors, especially for future applications. The results obtained for molecular organization, molecular relaxation dynamics, and electric polarization in the ion-conducting PNLCCs will be helpful for the optimization of their structure and performance. Promising ion-conducting PNLCCs were developed for thin-film electrical energy storage devices and as electrolytes for mini-batteries, solar cells, and solar-energy harvesting. Also, such electrolytic materials have a great potential for use in ionic devices for sensorics, mechatronics, and soft-electronics applications.

The major challenge regarding these electrolyte systems is to enhance their ionic conductivity at room temperature, and research efforts should be in this direction. The key factors for improvement of the ion conductivity and the ion transport through the included NLCs are clear—the increase of the amorphous portion in the polymer of PNLCCs and the formation of organized and highly efficient ion-conductive pathways. The latter can be performed by aligning approaches including an external force field and surface treatments. Increased ordering would provide a promising strategy for regulating ion-conductive pathways and alignment of charge carriers. The improvement of the synergy interplay between NLCs and the host polymer can enhance the efficiency of these ion conductors and will generate new applications. The current available reports indicate that by dealing with the composition of the PNLCCs one can achieve a controlled modification (tuning) of their structural, ion electrolytic, and dielectric properties. In this way by optimization of the composition, PNLCC electrolyte materials with improved ion transport and efficient dielectric response can be produced.

Despite the significant progress in the development of ion-conducting PNLCCs, their functionalities and applications have to be further explored, in particular toward biomedical and environment microanalytical sensor applications. In this context, the full understanding of physicochemical processes of electrostatic attraction-induced adhesion/adsorption of organic compounds and charged biomolecules on membranes made of such composites needs further studies.

The available knowledge on ion-conducting PNLCCs allows to conclude that these flexible soft-matter ion conductors are certain to play an important role in future advanced applications. We can expect new successful design strategies for development of novel ion-conducting PNLCCs, as well as new advances

toward their piezoresistive, flexo-dielectric, and flexo-ionic properties and related applications. Furthermore, devices with futuristic processes of operation based on ion-conducting PNLCCs are of great interest, as are the possibilities of using today's advanced film-forming technologies and additive manufacturing technologies, like 3D printing, to perform new architectural designs of these ion electrolyte composite materials.

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Notes

The author declares no competing financial interest.

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