Conductive Films Based on Composite Polymers Containing Ionic Liquids Absorbed on Crosslinked Polymeric Ionic-Like Liquids (SILLPs)

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Abstract

Polymerization of styrenic monomers containing imidazolium subunits in the presence of crosslinking monomers and using ionic liquids (ILs) as porogenic agents provides composite materials with excellent mechanical properties and displaying conductivities that are in the same order of magnitude than those shown by bulk ILs. This approach allows the use of high crosslinking degrees and low IL-loadings without compromising the required properties of the resulting composites. Besides, no appreciable leaching of the bulk IL component is detected.

Keywords: supported ionic liquids, ionic liquids, ionic conductivity, imidazolium, polymer electrolytes,

Introduction

The substitution of aqueous electrolytes by electrolytes based on ionic liquids (ILs) to obtain efficient polymer composite membranes has attracted significant interest in the last years [1]. This is due to the unique physical properties of ILs and their high ionic conductivity. Two main strategies have been explored for the preparation of polymeric composite membranes based on ILs. The first one involves the addition of an IL-phase into a polymeric matrix [2]. These membranes are generally prepared by direct polymerisation of a structural monomer and/or a crosslinking monomer in the presence of a room temperature IL (RTIL) or, alternatively by coating the corresponding polymeric membrane with the appropriate RTIL. In general, these procedures resulted in materials with good conductivities (ca. $10^{-2}$ S cm$^{-1}$ at room temperature) depending on the loading and nature of the IL and on polymer composition [3]. However, this approach presents some limitations due to the possible
leakage of the IL-electrolyte from the polymeric matrix. A second approach involves the use of the so-called polymerized ionic liquids (PILs) that can be obtained from monomers having ionic liquid-like structures [4]. They can be copolymerized with non-ionic comonomers leading to linear soluble PILs and/or with crosslinking monomeric agents leading to insoluble PILs [5]. Both, soluble and cross-linked poly(ionic liquid) materials have demonstrated to have interesting conductivity properties [6]. Indeed, their properties are highly dependent of the composition and type of the co-monomers used, as well as on the polymer morphology and the nature and length of the spacer linking the backbone and the ionic-liquid-like units [7]. Supported ionic liquid-like phases (SILLPs) have also been obtained by covalently binding IL-like moieties, such as alkylimidazolium cations, to either macroporous or gel-type polystyrene-divinylbenzene resins [8,9]. Partly related imidazolium resins based on polystyrene backbones have been used for different applications like gas separations [10-12]. However, their ionic conductivity drops significantly to values below 10^{-6} S cm^{-1} due to the decrease in the number of the mobile ions. An interesting alternative resides in the merging of both approaches [13,14]. Thus, a monomer bearing an ionic liquid-like fragment can be polymerized in the presence of an appropriate crosslinking agent and a RTIL. This provides a polymeric backbone containing IL-like moieties to which the IL molecules will be strongly associated. This approach can allow combining the advantages found for the two former alternatives and eliminating, or at least minimizing, the potential leaching of the bulk IL phase. Besides, the resulting properties of these composites, in particular their conductivity, can be tailored by the proper selection of the polymeric and liquid components, in particular by a selection of the elements defining the interaction between the different IL-based subunits (anions and cations). In this context, the use of ILs as porogenic agents has been demonstrated to be very useful for the preparation of monolithic macroporous polymers with tailored porous structures [15] and the polymerization of a combination of polymerizable divinilic ionic liquids with cellulose dissolved in an IL with has been investigated for the generation of new kinds of promising ion-gel-type composite materials [16].

Here we present our results on the synthesis and characterization of different crosslinked polymeric films bearing ionic liquid-like units in the polymeric network and obtained in the absence and presence of additional adsorbed ILs. Films with different IL/polymer ratios have been investigated, with the aim of understanding the influence of the interactions between the liquid and the solid ionic phase on the functional properties of the composites.

Experimental

Materials
All reagents were used as purchased from commercial suppliers without further purification. The liquid monomer 1 (VBIM [NTf2], 1-(4-vinylbenzyl)-3-butyl imidazolium bistriflamide) was synthesized following the procedure previously described [17]. Commercially available 1-butyl-3-methylimidazolium chloride ([BMIM][Cl] (2a) was purchased from Merck, while [1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide] [BMIM][NTf2] (2b) was prepared by the exchange of chloride by NTf2− using LiNTf2, according to the general experimental methodology described in the literature [18]. FTIR spectra were acquired with a MIRacle single-reflection ATR diamond/ZnSe accessory in a Jasco FT-IR 6200. Raman spectra were acquired on a JASCO NRS-3100 dispersive spectrometer under the following conditions: 785 nm laser with a single monochromator, grating 600 lines·mm−1, slit 0.2 mm, resolution 12.75 cm−1, with a center wavenumber of 1200 cm−1, a laser power of 90.1 mW, and ten accumulations of 5 s each. Elemental analyses were performed on a LecoTuSpect Micro instrument. Differential scanning calorimetry (DSC) analyses were obtained using a Mettler-Toledo 831-DSC device at 10 K/min, under a nitrogen atmosphere in the -70 to 80°C range.

**General procedure for the synthesis of the films F1-F3.**

A mixture of VBIM [NTf2] 1, trimethylolpropane trimethacrylate 3 and 1 wt % of AIBN (as the initiator) was stirred and ultrasonicated to obtain a homogeneous solution that was then cast into a glass mold. The solution containing monomers, cross-linkers, AIBN and IL was introduced in the narrow space created between two microscopy slides separated by two thin lamellas (see Figure 1). Polymerization was then carried out for 24 h at 65 °C in an oven. Afterwards, the films were removed mechanically from the molds and thoroughly washed with organic solvents. The resulting polymers were homogeneous, transparent and ca. 4-5 cm x 1.5-2 cm in size, with a thickness of about 130 ± 10 µm. Nitrogen elemental analysis was used to obtain the final IL-loading of the polymers. In all cases, the experimental nitrogen percentage obtained was in good agreement with the expected values.

**F1:** 60 wt % of VBIM [NTf2] 1 and 40 wt % of trimethylolpropane trimethacrylate 3. FT-IR (v cm⁻¹): 3146, 3119, 2965, 2887, 1719, 1464, 1350, 1328, 1182, 1132, 1055, 614. RAMAN (v cm⁻¹): 1637, 1613, 1449, 1420, 1351, 1330, 1267, 1242, 1208, 1188, 1136, 1117, 1056, 1027, 830, 744, 644, 616, 595, 574. IL-loading calculated by elemental analysis: 1.1 mmol IL/g of polymer (1.1 theoretical)(ca. 1 mmol of ions/mL) (Elemental analysis for N: experimental 5.2; calculated: 4.9 %).

**F2:** 70 wt % of VBIM [NTf2] 1 and 30 wt % of trimethylolpropane trimethacrylate 3. FT-IR (v cm⁻¹): 3152, 3115, 2966, 2937, 2879, 1725, 1564, 1346, 1321, 1182, 1131, 1051, 614.
RAMAN (ν cm⁻¹): 1630, 1613, 1450, 1421, 1354, 1329, 1268, 1242, 1207, 1188, 1136, 1118, 1056, 1027, 831, 743, 643, 614, 593, 574. IL-loading calculated by elemental analysis: 1.3 mmol IL/g of polymer (1.3 theoretical) (ca. 1.1 mmol of ions/mL) (Elemental analysis for N: experimental 5.7; calculated: 5.7 %).

F3. 77 wt % of VBIM [NTf₂] I and 23 wt % of trimethylolpropane trimethacrylate 3. FT-IR (ν cm⁻¹): 3152, 3107, 2966, 2938, 2882, 1725, 1564, 1346, 1268, 1241, 1207, 1187, 1135, 1117, 1056, 1025, 832, 742, 642, 614, 593, 573. IL-loading calculated by elemental analysis: 1.6 mmol IL/g of polymer (1.7 theoretical) (ca. 1.4 mmol of ions/mL) (Elemental analysis for N: experimental 6.7; calculated: 7.0 %).

**General procedure for the synthesis of films F4-F6.**

A mixture of VBIM [NTf₂] I, trimethylolpropane trimethacrylate 3, BMIM [NTf₂] 2a (F4 and F5) or BMIM [Cl] 2b (F6) and 1 wt % of AIBN (as the initiator) was stirred and ultrasonicated to obtain a homogeneous solution which was then cast into a glass mold. Polymerization was then carried out for 24 h at 65 °C in an oven. The films were separated from the glass plates and thoroughly washed with organic solvents and dried before use.

F4. 69 wt % of VBIM [NTf₂] I, 11 wt % of trimethylolpropane trimethacrylate 3 and 20 wt % of BMIM [NTf₂] 2a. FT-IR (ν cm⁻¹): 3153, 3147, 3107, 2965, 2938, 2877, 1725, 1564, 1346, 1321, 1182, 1131, 1051, 614. RAMAN (ν cm⁻¹): 1613, 1565, 1449, 1419, 1386, 1333, 1269, 1242, 1210, 1189, 1136, 1117, 1057, 1026, 830, 744, 643, 625, 575. IL-loading calculated by elemental analysis: 1.8 mmol IL/g of polymer (1.8 theoretical: 1.3 corresponding to the covalently supported imidazolium cations and 0.5 to the presence of 2a) (ca. 1.5 mmol of ions/mL) (Elemental analysis for N: experimental 7.5; calculated: 7.6 %).

F5. 58 wt % of VBIM [NTf₂] I, 8 wt % of trimethylolpropane trimethacrylate 3 and 34 wt % of BMIM [NTf₂] 2a. FT-IR (cm⁻¹): 3151, 3109, 3092, 2965, 2936, 2876, 1726, 1563, 1462, 1349, 1331, 1184, 1135, 1053, 738, 613. RAMAN (ν cm⁻¹): 1613, 1565, 1449, 1419, 1388, 1337, 1242, 1210, 1189, 1136, 1119, 1057, 1026, 830, 744, 645, 627, 606, 575. BMIM [NTf₂] IL-loading calculated by elemental analysis: 1.8 mmol IL/g of polymer (1.9 theoretical: 1.1 corresponding to the covalently supported imidazolium cations and 0.8 to the presence of 2a) (ca. 1.5 mmol of ions/mL) (Elemental analysis for N: experimental 7.6; calculated: 8.1 %).

F6. 59 wt % of VBIM [NTf₂] I, 8 wt % of trimethylolpropane trimethacrylate 3 and 33 wt % of BMIM [Cl] 2b. FT-IR (cm⁻¹): 3151, 3109, 3092, 2965, 2936, 2876, 1726, 1563, 1462, 1349, 1331, 1184, 1135, 1053, 738, 613. RAMAN (ν cm⁻¹): 1613, 1565, 1449, 1419, 1388, 1337, 1242, 1210, 1189, 1136, 1119, 1057, 1026, 830, 744, 645, 627, 606, 575. IL-loading calculated
by elemental analysis: 2.9 mmol IL/g of polymer (3.0 theoretical: 1.1 corresponding to the covalently supported imidazolium cations and 1.9 to the presence of 2a)(ca. 2.5 mmol of ions/mL) (Elemental analysis for N: experimental 9.3; calculated: 10.0 %; Elemental analysis for S: experimental 6.7; calculated: 7.2 %).

Impedance measurements.

Impedance measurements were carried out on the polymeric films at several temperatures lying in the range 273 K (0ºC) to 403 K (130ºC) and within the frequency window $10^{-1} < f < 10^7$ Hz. The experiments were performed with 100 mV amplitude, using a Novocontrol broadband dielectric spectrometer (Hundsangen, Germany) integrated by a SR 830 lock-in amplifier with an Alpha dielectric interface. The sample of interest was sandwiched between two gold circular electrodes coupled to the impedance spectrometer acting as blocking electrodes. The assembly membrane-electrode was annealed in the Novocontrol setup under an inert dry nitrogen atmosphere previously to the start of the actual measurement. For this, firstly a temperature cycle from 0ºC to 130ºC to 0ºC, in steps of 10ºC, was carried out. After this, in a new cycle of temperature scan, the dielectric spectra were collected in each step. This was performed to ensure the measurements reproducibility and to eliminate the potential interference of water retained by the composite membranes, in particular taking into account the hygroscopicity of some ILs. During the conductivity measurements, the temperature was maintained (isothermal experiments) or changed stepwise from 0 to 130ºC controlled by a nitrogen jet (QUATRO from Novocontrol) with a temperature error of 0.1 K during every single sweep in frequency.

Results and discussion.

Synthesis of poly(ionic) polymeric films. Polymerization of the styrenic monomer containing imidazolium fragments 1 was performed in the presence of trimethylolpropane trimethacrylate (TMPTMA, 3) as comonomer and crosslinking agent to obtain the corresponding poly(ionic) polymeric films F1-F3. The corresponding polymeric matrices differed on the degree of crosslinking associated to the content of 3 in the monomeric mixture (from 40 to 13% in weight). Films F4 and F5 were obtained in the presence an additional IL-phase. ([BMIM][NTf$_2$], 2a) (Scheme 1). In this case, the crosslinking degree ranged from 11 to 8% in weight (ca. 14-12% regarding the ratio monomer:crosslinker) and the amount of BMIM was adjusted to 20 and 34% of the total weight (see Table 1). Finally, F6 was prepared analogously to F5 but substituting [BMIM][NTf$_2$] (2a) by [BMIM][Cl] (2b).
All prepared polymers were fully characterized by a full set of spectroscopic tools as well as by elemental analysis and differential scanning calorimetry (DCS). Polymers F1-F3 gave excellent elemental analyses, with the values for all elements (C, H, N and S) within the accepted experimental error. The errors were slightly higher for F6 in the case of N, but not for the other elements. In the case of F4 and F5, the errors were higher for S, C and H, which must be associated with the difficult combustion of the bulk IL, being this behaviour dependent on the nature of the counteranion [19]. All prepared membranes were transparent, flexible, and could be easily cut into any desired size and shape or be bent with one pair of tweezers, even under dry conditions (see Figure 1). Interestingly, no appreciable leakage of the bulk IL was observed for polymers F4-F6 even after a prolonged treatment with organic solvents. More than 95% of the IL remained in the SILLP-composite after Soxhlet extraction. For this experiment, the corresponding weighted samples were extracted with a good solvent for the corresponding IL (CH2Cl2) during 48 h in a Soxhlet equipment and weighted again after vacuum drying. No weight loss was detected and the chemical characterization provided the same results than for the initial polymers.

**FT-Raman studies.**

Very small variations were observed in the FT-IR and RAMAN spectra for films of the first family (F1, F2 and F3) and also very small variations were detected within the second family of films (F4 and F5). The spectra obtained for F6 were also very similar to those of F4 and F5. However, more significant variations were observed when comparing both families of films, the one containing the IL absorbed in the matrix (F4-F6) and the other not containing such additive (F1-F3). Thus, for instance, Figure 2 shows the partial RAMAN spectra obtained for F2 and F4. It is interesting to note that for F4 the band at 1630 cm⁻¹ completely disappeared. This can be assigned to the absence of residual unreacted double bonds and is indicative of a higher degree of consumption of the polymerizable vinylic groups from 1. Thus, the presence of the porogenic IL, along with the much lower crosslinking degree, most likely provides a higher degree of mobility to the growing polymeric chains and facilitates the reaction of all the double bonds of the trifunctional crosslinkers. On the other hand, the appearance of new bands at 1388, 627 and 606 cm⁻¹ in F4 is clearly visible, which can be assigned to the presence of [BMIM][NTf₂] absorbed in the polymeric matrix [20].

Besides, the morphology of the membranes could be further characterized by optical and Raman microscopy. Optical microscopy images (Figure 3a) show that the surfaces of the films are not fully uniform and present some irregular patterns corresponding to areas protruding from the surface of the film.
However, a detailed study of these patterns through FT-Raman-mapping at several wavelengths, characteristic for the different components of the films (Figure 3b and 3c), suggests a uniform and compact distribution of the components within the different regions. The same changes in intensity are observed between the regions for the different bands studied and, thus, seem to correspond to the above mentioned physical heterogeneity more than to changes in composition.

**Differential scanning calorimetry studies.**

DSC curves were obtained for the different films at 10 K/min rate, under a nitrogen atmosphere, for the -70 to 80°C range. The corresponding thermograms are shown in Figure 4a. In order to properly analyze the DSC curves, the bulk ILs involved in the preparation of films F4-F6, namely [BMIM][NTf₂], 2a, ([BMIM][Cl], 2b, and the equimolecular mixture of both ILs were also studied under the same experimental conditions and the resulting DSC curves are presented in Figure 4b.

As could be expected for crosslinked PS-DVB polymers, which do not posses detectable Tg values, for the temperature range considered (-70 to 120°C, according to the conductivity studies to be carried out), the curves obtained for F1-F3 do not show appreciable transitions and present similar DSC curves, although some changes in the slopes are observed, due to the different chemical composition and crosslinking degree. The situation is clearly different for polymers F4-F6 containing absorbed bulk ILs. To properly understand the thermograms observed, the DSC analyses for the corresponding bulk ILs need to be considered. The DSC curve for [BMIM][NTf₂], 2a, is characterized by the presence of a small distinct endothermic peak at ca. -47°C, along with a significant change in the slope at -25°C in the cooling ramp and a very sharp slope change between -70 and -60°C in the heating ramp, a minor exothermic peak at ca. -23 is also observed. The DSC analysis for [BMIM][Cl], 2b, reveals the presence of a more defined structure, as could be expected from the higher coordinating ability of the anion, characterized by the presence of two well defined small exothermic peaks at -46 and 61°C in the heating ramp, along with a less defined transition starting at about -45°C in the cooling ramp reflected in a significant change in the slope of the curve. Interestingly the well-defined structure observed for [BMIM][Cl], 2b, is clearly lost in the equimolecular mixture with [BMIM][NTf₂], 2a. In this case, no defined peaks are observed, although the curve is dominated by similar slope changes to those observed in the case of 2a. In the case of F4, containing a 20% of 2a, the observed DSC displays some significant differences with those of both polymers F1-F3 and the bulk IL 2a. A more ordered structure is detected as suggested by
the changes in slope observed at ca. 25 and 40ºC in the cooling ramp and at ca. 40ºC in the heating ramp, not detected in the related F1-F3. In the case of F5, with a higher content of 2a (34% instead of 20%) and a lower crosslinking degree (8% instead of 11%), the DCS becomes more similar to that of the bulk IL 2a, being characterized by two important slope changes detected at 25ºC in the cooling ramp and at ca. -55ºC in the heating ramp. Nevertheless, the temperatures for these transitions are clearly different in both cases and the more defined peaks observed in the case of 2a are not detected in F5. As was observed in the case of the mixture of bulk ILs 2a/2b, the presence of chloride and bistriflamide salts in the composite film F6 is accompanied by a clear disruption of the more or less ordered structures found in the cases of F4 and F5 and the DSC curve becomes very similar to these obtained for F1-F3. Overall, the presence of a single bulk IL, containing the same counteranion present in the SILLP, absorbed on the porous structure of the macroporous SILLPs studied in this work can produce the presence of ordered monolayers of ILs deposited on the internal surfaces of the polymeric films. Such ordered structures seem to be absent, or at least significantly decreased, when the system is prepared in the presence of a mixture of counteranions for the SILLP and the bulk IL. Clearly this can have an important influence on the conductivity properties of these materials that are associated to the mobility of the corresponding ions.

**Electrochemical Impedance Spectroscopy.**

Electrochemical impedance spectroscopy (ISE) measurements were carried out for the samples Fi (i=1, 2, 3, 4, 5 and 6) at different temperatures in order to obtain information on their ion conductivity. The data were analysed in terms of their dielectric permittivity \( \varepsilon^* = \varepsilon' - j\varepsilon'' \), from which the imaginary part gives the conductivity (\( \sigma \)), as for a pure Ohmic conduction \( \varepsilon'' = \sigma/\varepsilon_0\omega \), where \( \varepsilon_0 \) represents the permittivity of vacuum and \( \omega \) the angular frequency of the applied electric field. The real part of the conductivity (\( \sigma' \)), is characterized on the high frequency side by a plateau, the value of which directly yields the dc conductivity, \( \sigma_{dc} \), and the characteristic radial frequency, \( \omega_c = 2\pi f_c \), at which dispersion sets in and turns into a power law at higher frequencies. On the other hand, the real part of the dielectric function \( \varepsilon' \) at \( f_c \) turns from the high frequency limit to the static value \( \varepsilon_s \). At lower frequencies, it is observed that \( \sigma' \) decreases from \( \sigma_{dc} \) and this is due to electrode polarization that results from blocking of charge carriers at the electrodes [21].

In Figure 5 the double logarithmic plots of the real and imaginary permittivity and conductivity (\( \varepsilon', \sigma', \varepsilon'' \) and \( \sigma'' \)) *versus* the frequency are given for all the samples at 50ºC.
From these figures we can observe three regions related with different behaviours of the samples: The low-frequency region of the spectrum is characterized by the electrode polarization (EP) where the formation of electrochemical double layers is satisfied. This frequency corresponds to the inflexion frequency in the double logarithmic plot of the real part of the conductivity (Figure 5d). Note that at this frequency a peak or a shoulder is observed in the log \( \varepsilon'' \) vs. log f plot (Figure 5b). This is a field of study of great interest in the case of ILs and related materials, such as the ones studied in this work, in order to explore their possible use as electrolytes for supercapacitors [22].

The region where a plateau regime is detected for the real part of the conductivity (Figure 5d) corresponds with the bulk dc conductivity \( \sigma_{dc} \), and, accordingly the conductivity of the SILLPs could be determined in this region, reflecting long-range ion transport. Finally, at higher frequencies, \( \sigma'(\omega) \) increases with increasing frequency. In this region the subdiffusive conductivity (SD) is obtained and corresponds to a dispersive regime containing information of localized movements of ions in the electrolytes [23]. The analysis of this part of the spectra is, however, beyond the scope of this study.

From the log-log plot of \( \varepsilon' \) versus frequency given in Figure 5a at 50°C of temperature, it can be observed that the dielectric strength increases with the loading of the IL-like fragments (BMIN [NTF_2] like units) covalently attached to the polymeric network. This is easily realized when comparing the samples F1 and F2 with F3, which contains the highest loading (87%) of IL-like fragments, in particular for lower frequencies. This increment is more pronounced in the case of films containing ILs absorbed in the matrix (F4, F5 and F6). For F4-F6 the values of the dielectric strength at lower frequencies follow the trend expected for the total content in IL fragments (bulk IL 2+ monomeric IL 1, see Table 1), while at higher frequencies the observed values follow the order associated to the content in bulk IL (2).

In general the dielectric strength follow the order F1<F2<F3<F4<F5<F6. This behaviour is not exclusive of this temperature but is maintained for the whole range of studied temperatures, indicating that the amount of transporting anion present is associated to an increasing of the strength.

As an illustration, the plots of log \( \sigma' \) and log \( \sigma'' \) vs. log f are shown in Figure 6 for the sample F6 for all the range of temperatures studied. The representation of both the real and the imaginary components for such a large frequency range allows to easily visualizing the presence of two different processes: charge transport for \( ca. 10^2 \) to \( 10^6 \) Hz, and electrode polarization (EP) occurring at lower frequencies. It can be observed that the electrode polarization (EP) and the bulk charge transport are strongly dependent on the temperature. A
similar behaviour was found for the other samples \( F_i \) (\( i=1, 2, 3, 4, 5 \)). Such performance has also been found in bulk imidazolium ionic liquids by other researchers [24].

A close inspection of data in Figure 5a, corresponding to the double logarithmic plot of \( \log \varepsilon' \) vs. \( \log f \) for \( F_6 \), shows that, at high frequencies, in the range \( 10^6 \) Hz to \( 10^7 \) Hz range, \( \varepsilon'(\infty) \approx 17 \). This observed value is slightly higher than those reported as typical for many ionic liquids and glasses whose conductivity is characterized by the mobility of \( \text{NTf}_2^- \) ions, where the value of permittivity varies between 6 and 11 at 50ºC [25]. The static dielectric permittivity values calculated by dielectric relaxation spectroscopy for a series of dialkylimidazolium bistriﬀlamides at 25ºC ranged between 12 and 15, being of the same order for other aprotic ILs and much higher for protic ILs [26]. It is worth mentioning that in our case the calculated dielectric constants range from 6 to 17 at 50ºC, the observed value being very similar for films \( F_1-F_3 \), but clearly higher for the films \( F_4-F_6 \) containing absorbed bulk ILs.

For this dielectric constant range, the Bjerrum length is about 3 nm. In this situation several rearrangements of neighbouring fragments and ions must take place and this value is presumably the dielectric constant more relevant to analyse the potential use of the developed materials in a macroscopic capacitor. In the case of the films studied in this work, the trend observed for the values of the static permittivity (\( F_1<F_2<F_3<F_4<F_5<F_6 \)) is clearly related to their chemical composition. The corresponding values range from 6 (\( F_1 \)) to 17 (\( F_6 \)). The dielectric relaxation strength \( \varepsilon'(0) - \varepsilon'(\infty) \), is a measure for the dipole fluctuation due to fast processes, and from there the mean square displacement of the anions in the samples \( F_1-F_6 \) can be estimated according the following equation [23b].

\[
\langle R^2(\infty) \rangle_{cr} = \frac{6k_BT\varepsilon_0}{N_q^2} [\varepsilon'(0) - \varepsilon'(\infty)]
\]

(1)

Where \( q \) is the ionic charge, \( \varepsilon_0 \) denotes the permittivity of the free space, \( N_q \) the average number density of the charges (for simplicity, \( N_q \) for \( \text{NTf}_2^- \) has been used for all cases, assuming that \( \text{NTf}_2^- \) is the most relevant anion for all the samples). From eq. (1) values ranging from 4 to 7 Å were obtained for the mean square displacement of the anions. These values are close to the diameter calculated for the imidazolium cations and the \( \text{NTf}_2^- \) anions, and very close to the values observed by Huber et al. [27].

When normalizing the results with respect to the dc conductivity (\( \sigma_{dc} \)) and the electrode polarization frequency \( f_c \), it is remarkable that a coinciding plot is obtained for all the samples for the whole range of temperatures studied, as illustrated in Figure 6 for \( F_6 \). As seen in Figure 6 (bottom graphs) the isotherms superpose rather well over the isotherm of reference. Notice that the master curve extends over roughly 10 decades. Similar results are found for the other
samples. This implies the existence of a single charge transport mechanism for all the samples studied in this paper.

From the Bode diagram [28] shown in Figure 6 (left graphic on the top) for the sample F6, the conductivity of the sample at all the studied temperatures can be obtained. The pertinent results are given in Table 2. In Figure 7, the values of the conductivity for all the samples as a function of the temperature are represented. The data show a Vogel-Fulcher-Tamman-type behaviour, which is typical for the majority of polymers at temperatures above Tg. For all temperatures studied the values of $\sigma$ increase with the temperature, following the order $\sigma(F6)>\sigma(F5)>\sigma(F4)>\sigma(F3)>\sigma(F2)>\sigma(F1)$. As observed in Figure 7, the dc conductivity increases when the amount of the crosslinker (3) decreases, as this is associated simultaneously to a higher mobility of the polymeric chain and to an increase in the loading of IL-like fragments covalently attached to the polymeric matrix. On the other hand, when the amount of the bulk IL (2a) increases from 20% (F4) to 34% (F5) the conductivity also increases. For example, at 50°C the value changes from $2.3x10^{-5}$ S/cm for F4 to $6.6x10^{-5}$ S/cm for F5. Taking into account that the total loading of imidazolium units (mmol/g, considering both the bulk IL 2a and the fragments covalently attached originating from 1) is very similar for F4 and F5, these results indicate a clearly higher contribution to the final conductivity from the bulk IL. This is also in good agreement with the significant differences observed in conductivity between F3 and F4, differing less in total loading than F2 and F3. Finally, when the ion NTf$_2^-$ in the component 2a is replaced by the anion Cl$^-$ (component 2b) the dc conductivity increases further, for the same loading and crosslinking degree, reaching a conductivity value of $1.9x10^{-3}$ S/cm for F6 at 100°C. A general comparison between all the samples for the whole range of temperatures shows, for instance, that the dc conductivity of F6 increases from $8.25x10^{-6}$ S/cm at 0°C to $3.5x10^{-3}$ S/cm at 130°C, while in case of the sample F1 this increase is from $9.1x10^{-11}$ S/cm to $1.84x10^{-5}$ S/cm for the same temperature range. As can be observed, this represents a huge increase in conductivity, in particular at low temperatures (up to 5 orders of magnitude) obtained through a proper selection of the overall components and structure of the corresponding SILLP films.

As seen in Figure 7, the addition of 20% in weight of the IL component 2a containing the NTf$_2^-$ anion, produces an increase of two orders of magnitude in the conductivity for all the range of temperatures with respect to the samples F1, F2 and F3 obtained from different monomeric mixtures but not containing any bulk IL. When the amount of NTf$_2^-$ anion increases to 34%, sample F5, the conductivity further increases, being almost three times higher for F5 than for F4. Finally, when the anion of the bulk IL changes from NTf$_2^-$ to Cl$^-$, the conductivity still increases two times, (see table 2). These changes can clearly be related with the
modification observed above in the thermal behaviour of these composites and the corresponding degree of ordering. It is interesting to compare the present results with those obtained, for instance, for a linear ABA triblock copolymer poly(styrene-b-[1-ethyl-3-(4-vinylbenzyl)imidazolium bis(trifluoromethane sulfonyle)imide]-b-styrene) for which a value of ca. $5 \times 10^{-7}$ S cm$^{-1}$ is observed around 40 ºC, reaching a maximum measured value of about $3 \times 10^{-4}$ S cm$^{-1}$ around 150 ºC [29]. Taking into consideration the important changes in polarity and hygroscopicity associated to the change in the anion from NTf$_2^-$ to Cl$^-$ [8a], the presence of retained water could have an influence on the conductivity observed. Although the experimental protocol used was set-up to eliminate the water present in the composites, by carrying out an initial cycle (0ºC to 130ºC to 0ºC) before each measurement, this effect cannot be completely ruled out, if water molecules strongly associated to the IL fragments are present. On the other hand, it is also important to consider the changes often observed for the properties, including conductivity, of mixtures of ILs that can clearly deviate from linearity [30].

A close inspection of the variation of the values represented in the activation plot of Figure 7 allows obtaining the temperature dependence of the charge transport values, according to the Vogel-Fulcher-Tammann equation

$$
\log \sigma = \log \sigma_\infty - \frac{B}{T-T_0}
$$

(2)

Where B is a fitting parameter related with the curvature of the plot that can be seen as the high temperature activation energy of the process underlying the conductivity $\sigma_{dc}$. $T_0$ is the Vogel temperature, considered as the one at which the relaxation time would diverge and $\sigma_\infty$ is a pre-factor related with the limit conductivity at higher temperatures. In Table 3 the corresponding values obtained for the parameters $\sigma_\infty$, $T_0$ and B are gathered. In the same table the values found for the activation energy have also been tabulated.

The values of the activation energy follow the trend $F_1>F_2≈F_3>F_4≈F_5>F_6$ being in most cases smaller than the values obtained for imidazolium-based ionic liquids in aqueous solutions, where the activation energy was about 19 kJ/mol [31]. This indicates that excellent ion mobilities can be obtained with these films in comparison with the aqueous solutions of similar ILs. The comparison of $F_1$ and $F_2$ reveals that a decrease in the crosslinking with the associated increase of the IL-like loading, and accordingly the improvement in the mobility of the polymeric chains and the attached functional groups, is clearly accompanied by a decrease in $E_{act}$. However, this effect seems to reach a limit for a value of crosslinking around 30%, as a
further decrease up to 13% in F3 (and the increase in IL-like fragments loading from 1.3 to 1.6 mmol/g) is not accompanied by a significant decrease in the value of $E_{act}$. The incorporation of bulk ILs to the composite films is associated to a larger decrease in $E_{act}$ than those observed for the changes in the monomeric composition. Thus, F4 and F5 show $E_{act}$ values that are half than those for F3. However, the increase in the amount of the IL 2a from 20% to 34% is not accompanied by an appreciable decrease in this parameter. On the other hand, the exact nature of the IL, and particularly the nature of the anion, is critical. Changing the anion from NTf$_2^-$ to Cl$^-$, using 2b in F6, produces a further decrease in $E_{act}$ by about 10%. As expected, these results are in excellent agreement with the values obtained for the dc conductivities.

**Diffusion coefficients and charge concentration.**

In binary salt/polymer solutions both anions and cations can be mobile, since most of them may be interacting forming ion pairs or clusters. According to this, the concentration of the mobile charges involved can be difficult to calculate. However, the total concentration of the charge carrier can be estimated following the procedure described by Sorensen and Compañ [32], limiting the generalization of the Trukhan model based on the Nernst-Planck equations of electrodiffusion, where the electrolyte considered is a binary system and the diffusion coefficients in the same phase may be different [33,34]. This approach has also been used to model the electrode polarization in the case of ionomers with anions fixed along the polymer chains and the cations as mobile counterions [35]. This is clearly a good model for the systems here considered, as the samples under study contain ionomers with cations fixed along the polymer chains and anions like NTf$_2^-$ or Cl$^-$ can move easily along the polymer.

The model allows to make an estimation of the diffusion coefficients and the concentration of the free charge (mobile ion) carriers from the values of the maximum of loss tangent ($\tan \delta$), where $\delta$ is the phase angle of the complex dielectric permittivity, $\varepsilon^*$. Assuming a 1:1 stoichiometry for the electrolyte, with equal diffusion coefficients, and the film to be “thick” compared with the Debye length, the diffusion coefficients for the anion, $D_a$, and cation, $D_c$, ($D_a = D_c$) can be estimated according to equation (3) [32-34,36].

$$D = \frac{2\pi f_{max} L}{32 \left[(\tan \delta)_{max}\right]}$$  \hspace{1cm} (3)

Where $f_{max}$ is the value of the frequency corresponding to the maximum of the loss tangent, $L$ is the thickness of the sample and $(\tan \delta)_{max}$ the value of the loss tangent at the maximum of the spectrum. When the Maxwell-Wagner-Sillars (MWS) effects dominate completely over the effects of the surface polarization at low frequencies and the internal relaxations in the polymer
(moderate and high frequencies) are present, then the plot of log \((\varepsilon'')\) vs. log \(f\) yields a straight line with slope -1 over an extended range of intermediate frequencies (see figure 5b). This is a clear indication of a MWS behaviour and from the intersection of this line with log \(f = 0\) we can estimate the conductivity. Identically, in the plot of the log \((\sigma')\) vs. log \(f\) a plateau is observed in the same range of frequencies for which log \((\varepsilon'')\) vs. log \(f\) displays a straight line with slope -1. From this plateau we could obtain the dc-conductivity and the pertinent results following this procedure were presented in table 2.

Figure 8 shows the values of tan \(\delta\) as a function of the perturbation frequency, at 50\(^\circ\)C, for all the samples studied. Well defined single maxima in tan \(\delta\) appearing at different frequencies in each case, can be observed. The frequency for the appearance of such a maximum is dependent on the working temperature as is illustrated in the inset of the figure displaying the results found for \(\text{F4}\) in all the range of temperatures. A similar behaviour has been observed for the other SILLPs. As can be seen in the inset for the sample \(\text{F4}\), the relaxation strength increases slightly with temperature and as the temperature increases the frequency of the maximum shifts to higher values. The same trend is also detected for the other samples.

As observed in Figure 8, the intensity and the frequency of the peaks is very sensitive to the different structural elements present in the SILLPs and composites studied. Thus, both the intensity and the frequency of the peak are quite similar for \(\text{F1}\) and \(\text{F2}\) even if the loading of covalently attached ionic fragments for the second is higher (70% of imidazolium monomer 1 instead of 60% or 1.3 vs. 1.1 mmol/g) and, accordingly, the crosslinking is lower (30% of monomer 3 instead of 40%). However, a large increase in the value of tan \(\delta\), from ca. 5 to ca. 20, is observed for \(\text{F3}\) in which the loading has increased to 1.6 mmol/g (87% of monomer 1) and the crosslinking decreased to 13%. The position of the maximum is concomitantly shifted to higher frequencies. This seems to suggest that there is minimum value of loading or a maximum value of crosslinking (or both) required to reach significant values of tan \(\delta\). An additional increase in diffusivity to a value of ca. 40, and an accompanying shift to higher frequencies, is observed for \(\text{F4}\) where the covalently attached IL-like fragments of \(\text{F3}\) are partly substituted by a related bulk IL (2a), which maintains almost unchanged the crosslinking degree but increases the molar loading of the film from 1.6 to 1.8. Rather surprisingly, a further increase in the percentage of the bulk IL adsorbed in the SILLP, but maintaining constant the total ion loading in 1.8 mmol/g, giving place to \(\text{F5}\), is not accompanied by an additional increase in the maximum value of tan \(\delta\). On the contrary this value is reduced to ca. 25, although the frequency of the maximum is still shifted to higher values. This could be associated to appreciable changes in relaxation times. Interestingly the change of the NTf\(_2^-\) counter anion for \(\text{Cl}^-\) also has an effect. Thus, \(\text{F5}\) and \(\text{F6}\) only differ in their weight
composition in the fact that \textbf{F5} is prepared using \textbf{2a} (NTF$_2^-$ counter anion) as the porogenic bulk IL, while \textbf{2b} (Cl$^-$ counter anion) is used for \textbf{F6}. This leads to a modification of the anions present and to an increase in the total ion loading (2.9 vs. 1.8 mmol/g). A significant increase in the maximum value of $\tan \delta$ is observed for \textbf{F6} (from ca. 25 to ca. 35) although no shift in the frequency is observed.

The inset in Figure 8 shows the temperature dependence of $\tan \delta$ for \textbf{F4} from 0ºC to 130ºC that reveals that the relaxation strength increases slightly with temperature. On the other hand, the representation of the eletrode polarization time $\tau_{EP}$ as a function of the reciprocal of the temperature (Figure 9) presents a curve that, in general, cannot be described through a simple Arrhenius fit, indicating that in the considered SILLPs and composites a simple dependence with the temperature is not present. Taking into account that $\tau_{EP}$ represents the mean time for an ion to travel from one electrode to another, at times longer than $\tau_{EP}$ a large quantity of mobile ions will have built up at the electrodes and the dependence with temperature of ion mobilities will not present an Arrhenius behaviour, as will happen with the conductivity (see Figure 7). Similar results have been found for poly(ethylene oxide) based sulfonated ionomers having different cations such as Li$^+$, Na$^+$ and Cs$^+$ [33]. As can be see in Figure 9, the polarization times increase with the decrease in the loading of IL-like fragments (compare, for instance samples \textbf{F1} and \textbf{F3}). Nevertheless, the most critical factor seems to be the presence of bulk ILs adsorbed on the polymeric matrix. In general, the presence of bulk ILs produces a decreasing of the values of $\tau_{EP}$ that can be up to 2-3 orders of magnitude smaller for \textbf{F4-F6} than for \textbf{F1-F3} at the same temperature. Comparing \textbf{F4} and \textbf{F5} reveals that an increase in the amount of absorbed IL produces an additional decrease in the polarization times, in particular at lower temperatures, with the corresponding values converging at high temperatures. The comparison between \textbf{F5} and \textbf{F6} suggests that the change in the counter anion of the bulk IL from NTF$_2^-$ to Cl$^-$ is not significative at low temperatures but above ambient temperature, the polarization times decrease more rapidly for \textbf{F6} than for \textbf{F5}, which suggests that the counter anion of the bulk IL affects the frequency at which the polarization starts to be present in the system and, accordingly, is affected by its chemical nature.

From the data previously obtained, and using the eq. (3), the diffusion coefficients for the different SILLPs can be obtained as a function of the temperature. The corresponding plots are presented in Figure 10. From the analysis of our results it can be observed that the diffusion coefficients can be very much affected by different structural parameters of the films. This is particularly evident at lower temperatures, where the corresponding coefficients can differ by almost 5 orders of magnitude. In all cases, the diffusion coefficients increase with the temperature, but this effect is more pronounced for samples \textbf{F1-F3} having solely ionic
fragments with the cations covalently attached to the polymeric network. In this case, the diffusion observed must involve the hoping of the anions and can have a significant contribution from the dynamic of the polymeric chains. From the results we can see that the most remarkable effect of the temperature is observed for F3, the polymer of this family containing the lower crosslinking degree and the higher loading of ionic fragments. Thus, these changes with temperature seem to reflect the increased mobility of the polymeric chains containing the ionic groups. The presence of bulk ILs adsorbed on the polymeric matrix seems to reduce the effect of the temperature on the diffusion coefficients. This suggests that, in these cases, the contribution of the bulk IL to the diffusion coefficients is predominant. For most of the temperature range studied, except for the higher temperatures, F5 and F6, the polymers containing a larger amount of bulk IL, are the films displaying higher values of the diffusion coefficients. It must be noted that the curves for F5 and F6 are very similar, although the values for F5 are always slightly higher than those for F6. Although the weight composition of both composites is similar (table 1) the total ion loading for F6 is significantly higher (2.9 vs. 1.8 for F5) and this corresponds to a higher molar loading of the bulk IL (1.9 mmol/g vs. 0.8 mmol/l for F5). Accordingly, one could expect the reverse trend in the observed values of the diffusion coefficients, with the values for F6 being constantly higher. Thus, the nature of the anion in the bulk IL (NTf₂⁻ in F5 and Cl⁻ in F6) seems to play an important role for this parameter.

The measured conductivity is the sum of the total contributions of the charge carriers, cations and anions, assuming that all the available ions participate in the ionic transport. From the experimental results we have estimated the total conductivity and its value can be associated to the maximum possible contribution of the cations [37]. The ionic conductivity is related with the diffusion coefficient and the mobile ion concentration, \(c_{\text{ion}}\), by the equation (4),

\[
\sigma_{dc} = \frac{F^2}{R \cdot T \cdot N_A} c_{\text{ion}} \cdot D
\]

In this equation, \(\sigma_{dc}\) represents the ionic conductivity determined from the Bode diagrams [28] obtained from the dielectric spectra at the frequency where the tangent of the dielectric loss angle presents a maximum, (i.e. the dc-conductivity), as is shown in figure 5, D is the diffusion coefficient obtained following the procedure described above, R is the gas constant, F is the Faraday constant, \(N_A\) the Avogadro number and T the absolute temperature. Using this equation, the theoretical charge carrier density (i.e. free ion concentration) in the samples, as a function of the temperature, can be estimated. The corresponding results are represented in Figure 11. The results obtained show that the lower charge carrier density corresponds, as
could be expected, to the films containing solely imidazolium subunits covalently attached to the polymeric matrix (F1-F3). As was discussed in the case of the tan δ values, F1 and F2 present a very similar behaviour, while F3 having a higher loading of ionic fragments and a lower crosslinking degree presents values for this parameter that are 1-2 orders of magnitude higher than those for F1-F2. The presence of adsorbed bulk ILs is associated to an increase in the charge carrier density. A comparison between F4 and F5 shows that the increase from 20% to ca. 30% in the amount of bulk IL (2a), keeping essentially constant the total loading of IL-units, is accompanied by an increase of the values of about 1 order of magnitude. Very interestingly, for F6, structurally similar to F5 but having Cl⁻ instead of NTf₂⁻ as the counter anion of the bulk IL (2b), the calculated charge carrier density is smaller than that for F5. This must be associated to the lower dissociation degrees present in F5 according to the more coordinating nature of the Cl⁻ anion. It must also be noted that while F1-F2, and F4-F6 display a clear variation of the values obtained with the temperature, they are almost invariable for F3 for the whole temperature range studied.

Conclusions.
Films prepared from SILLPs represent a very useful approach for conductive membranes. Significant conductivities can be achieved through a fine tuning of the structure of the SILLP, in particular when bulk ILs are incorporated as porogens that become strongly associated to the functional polymeric surfaces and do not leach under a variety of conditions (> 95% retained after Soxhlet extraction). Both, the nature and degree of the crosslinking and the loading and structure of the IL moieties and the bulk IL, in particular the nature of the anion, are key parameters to understand the conductivities obtained.

It is important to note that the present approach, involving the polymerization of a styrenic imidazolium derivative and other(s) comonomer(s), including the corresponding crosslinking agents, in the presence of a bulk IL acting as the porogenic agent allows the preparation of composites based in polymers with relatively high crosslinking degrees (ca. 10%). In comparison with other approaches requiring polymers only lightly crosslinked, this allows the preparation of materials with good mechanical properties (i.e. mechanical stability, flexibility, shape persistence, etc) but, at the same time, providing excellent conductivity parameters that can be compared with those determined for bulk ILs. In this regard, conductivities reported at room temperature for bulk ILs can be up to two orders of magnitude higher than those obtained in our composites. Thus, for BMIM [NTf₂] a value of 3.9 × 10⁻³ S cm⁻¹ has been reported [36], and a value of 0.25 × 10⁻³ S cm⁻¹ has been calculated for BMIM [Cl] at 40 ºC. For the corresponding composites containing BMIM [NTf₂] (F4 and F5), conductivities at 20 ºC are
0.15 $10^{-5}$ and 0.54 $10^{-4}$ S cm$^{-1}$ respectively. Remarkably, for the composite (F6) containing BMIM [Cl] at 40 ºC the value obtained is 0.17 $10^{-3}$ S cm$^{-1}$, which is almost identical to the value for the related bulk IL. It is important also to note that very important increases in conductivity can be achieved with a moderate increase in temperature. In this way, at 80 ºC, the conductivity values for F4-F6 increase 1-2 orders of magnitude relative to those at room temperature.

Besides, this can be achieved just using a limited amount of bulk IL (ca. 20-30%) in the preparation of the corresponding composites. The conductivity values achieved at operational temperatures for IL-SILLP based composites (F4-F6) compare well with those reported for other IL/polymer and IL/PIL blends and those observed for many proton exchange membrane fuel cell (PEMFC) polymeric electrolytes and other electrolytic systems for electrochemical devices such as supercapacitors and batteries [3]. This opens the way to the study of these materials, under the appropriate conditions allowing practical ionic conductivities, for this purpose. An illustrative comparison can be made with values reported for the non-crosslinked benchmark PIL poly(1-vinyl-3-ethylimidazolium) [NTf$_2$] for which different studies have reported values of 6.3 $10^{-7}$, 2.5 $10^{-11}$ and 5.0 $10^{-5}$ S cm$^{-1}$ at 20-30 ºC [39], or with the related polystyrene derived PIL poly(styrene-b-[1-ethyl-3-(4-vinylbenzyl)imidazolium bis(trifluoromethane sulfonyl)imide]-b-styrene) (ca. 5 $10^{-7}$ S cm$^{-1}$ at ca. 40 ºC) [29]. In general, high loadings of bulk ILs, ranging from 40% to 200%, are required to obtain acceptable conductivities, even in IL/PIL composites, in particular for crosslinked polymers [39c,40]. High IL-loadings, however, compromise the mechanical stability and the practical applicability of many of those systems as solid electrolytes. This is not the case of the composites here considered, which, as mentioned, can be prepared as crosslinked polymeric PILs with good mechanical properties containing moderate amounts of bulk ILs. The results here presented reveal that a fine tuning of the properties of these SILLP-based polymeric composites is possible through an appropriate design of the different structural parameters. The modular nature of these structural parameters at both the polymeric matrix and the bulk IL greatly facilitates the corresponding optimization process and opens the way to the preparation of new families of conductive polymeric materials for further applications in different fields, in particular in energy-related areas.

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References


Table 1. Chemical Composition of the Films and theoretical and experimental ion loading

<table>
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<tr>
<th>Entry</th>
<th>Film</th>
<th>Composition % weight</th>
<th>Exp. loading in mmol/g (theor. loading)</th>
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<td></td>
<td>1  IL  3</td>
<td>1  IL</td>
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<td>F1</td>
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<td>1.6 (1.7)</td>
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<tr>
<td>4</td>
<td>F4</td>
<td>69 20$^a$ 11</td>
<td>- (1.3) - (0.5)$^a$</td>
<td>1.8 (1.8)</td>
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<tr>
<td>5</td>
<td>F5</td>
<td>58 34$^a$ 8</td>
<td>- (1.1) - (0.8)$^a$</td>
<td>1.8 (1.9)</td>
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<td>6</td>
<td>F6</td>
<td>59 33$^b$ 8</td>
<td>1.1 (1.1)$^c$ 1.8 (1.9)$^b$</td>
<td>2.9 (3.0)</td>
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</table>

$^a$ IL 2a; $^b$ IL 2b; $^c$ The experimental total ion loading has been calculated from the data of %N experimental, the theoretical loadings according to the composition are given in parentheses; $^d$ The experimental loading of 1 in film F6 has been calculated from the data of %S experimental.
Table 2. Conductivity values obtained from the Bode diagrams for all the SILLPs at the different temperatures studied

<table>
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<tr>
<th>T (ºC)</th>
<th>F1 σ(S/cm)</th>
<th>F2 σ(S/cm)</th>
<th>F3 σ(S/cm)</th>
<th>F4 σ(S/cm)</th>
<th>F5 σ(S/cm)</th>
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<td>$T_0$ (K)</td>
<td>$E_{\text{act}}$ (kJ/mol)</td>
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<tr>
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Figure captions

Scheme 1 Synthesis of films F1-F6 (1% AIBN, 65 °C, 24 h).

Fig. 1. Procedure for the preparation of polymeric films. Appearance of a representative film.

Fig. 2. Partial RAMAN spectra for the films F4 (black line) and F2 (grey line).

Fig. 3. Optical microscopy (a, 16x, bottom, x 32x, top) and FT-Raman mapping of a sample of F4. Mapping images b and c were obtained by measuring the intensity of the bands at 1615(b) and 743 cm\(^{-1}\) (c)

Fig. 4. DSC thermograms for the films F1-F6.

Fig. 5. Double logarithmic plots of the real and imaginary permittivity and conductivity (\(\varepsilon', \sigma', \varepsilon''\) and \(\sigma''\)) versus frequency for all the samples at 50°C.

Fig. 6. General Behavior of the sample F6 at different temperatures. (Top): double logarithmic plots of \(\sigma'\) and \(\sigma''\) vs. frequency. (Bottom): master curve of the normalized plots respect to the real and imaginary parts of the conductivity.

Fig. 7 Representation of the conductivity as a function of the reciprocal of the temperature for all the samples studied. The solid line represents the fit to a Vogel-Fulcher-Tammann behaviour.

Fig. 8 Representation of tan \(\delta\) vs. frequency for F1 - F6 at 50 °C. The inset shows the temperature dependence of this plot for F4 (from 0°C to 130°C).

Fig. 9 Temperature dependence of the electrode polarization time \(\Box_{\text{EP}}\).

Fig. 10 Arrhenius plots for the diffusion coefficients obtained according the Truham model (Eq.(3)) for the different SILLPs

Fig. 11 Variation of the charge carrier density of the mobile ion vs. the reciprocal of the temperature for all the samples studied.