Guar gum as biosourced building block to generate highly conductive and elastic ionogels with poly(ionic liquid) and ionic liquid

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A B S T R A C T
In this study, we report on the simple and straightforward preparation of ionogels arising from the addition of guar gum (a plant-based polysaccharide) in a solution of precisely-defined poly(ionic liquid) chains (PIL) in imidazolium-based ionic liquid (IL). The development of intermolecular polar interactions (mainly hydrogen bonds) and topologic chain entanglements induces the formation of physical biohybrid ionogels, whose elastic properties can be easily tuned by varying the composition (up to 30000 Pa). The combined presence of guar gum and PIL confers excellent dimensional stability to the ionogels with no IL exudation combined with high thermal properties (up to 310 °C). The resulting materials are shown to exhibit gel scattering profiles and high conductivities (> 10−4 S/cm at 30 °C). The benefit linked to the formation of guar/PIL associations in IL medium enables to find a good compromise between the mechanical cohesion and the mobility ensuring the ionic transport.

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1. Introduction

Ionogels are an emerging class of functional materials arising from the successful marriage of an ionic liquid (IL) and an inorganic, hybrid or polymer matrix (Le Bideau, Viau, & Vioux, 2011; Marr & Marr, 2016; Ye, Rick, & Hwang, 2013). Exploitation of this hybridization approach allows for overcoming recurrent issues encountered with molecular ILS in the field of material sciences (inferior mechanical properties and strong IL leakage due to the liquid behavior of ILS) without jeopardizing their inherent attributes (good chemical and thermal stability, non-flammability, negligible vapor pressure, wide electrochemical window and high ionic conductivity) (Hyes, Warr, & Atkin, 2015). Such combination is very relevant from fundamental aspect (Kimizuka & Nakashima, 2001; Kitazawa et al., 2016) and opens high perspectives in numerous fields of application, i.e. energy, sensing, catalysis and so on (Liu et al., 2014; Wu et al., 2016; Zhong et al., 2015). Notably, ionogels have attracted considerable interest for the design of solid-state electrolytes which requires finding a good compromise between (ion) mobility (a crucial feature for obtaining high conductivity), thermal and mechanical properties, and dimensional stability (without IL exudation) (Ye et al., 2013). Synthetic routes for preparing ionogels can be classified into two main categories: i) chemical ionogels stemming from the polymerization of multifunctional (co)monomers and/or the cross-linking of polymer chains in IL medium (Matsumoto & Endo, 2009; Susan, Kaneko, Noda, & Watanabe, 2005; Visentin, Dong, Poli, & Panzer, 2014) or the preparation of hybrid organic-inorganic networks (Gayet et al., 2009; Kato, Okazaki, & Hayase, 2005; Néouze, Le Bideau, Gaveau, Bellayer, & Vioux, 2006) and ii) physical ionogels based on ionic liquids and macromolecular gellers (Kimizuka & Nakashima, 2001). Physical ionogels have been extensively explored lately because these materials can be simply prepared through the mixing of IL and polymers. For this purpose, various synthetic homopolymers, such as poly(ethylene oxide), poly(methyl methacrylate), poly(vinylidene fluoride-co-hexafluoropropylene), poly(vinyl alcohol), Nafion® and silicone (Brown et al., 2010; Chen et al., 2007; Horowitz & Panzer, 2014; Jiang, Gao, Li, & Su, 2006; Lewandowski & Swiderska, 2004; Mok, Liu, Bai, Lei, & Lodge, 2011; Shalu & Singh, 2015; Zebbe et al., 2016) and copolymers, such as poly(styrene-b-ethylene oxide-b-styrene) (He, Boswell, Bühlmann, & Lodge, 2007) have been blended with ILS. Biosourced polymers such as polysaccharides have also been used to develop ionogels with reduced environmental impact due to the non-toxicity and renewable character of the host polymer matrices. In this frame, one can cite the

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pioneering works of Kadokawa and Prasad who prepared physical ionogels from imidazolium ionic liquids and cellulose, chitin, xanthan gum, or carrageenan (Izawa & Kadokawa, 2010; Kadokawa, Murakami, & Kaneko, 2008; Prasad, Kaneko, & Kadokawa, 2009; Prasad, Murakami et al., 2009). The same group also described the construction of ionogels from polymerizable ionic liquids, ILS (as processing-aids) and polysaccharides (cellulose (Murakami, Kaneko, & Kadokawa, 2007), chitin (Setoyama, Kato, Yamamoto, & Kadokawa, 2013) and fengnue gum (Kadokawa, Kato, Setoyama, & Yamamoto, 2013)) using radical polymerization procedures. After polymerization, the IL initially introduced to dissolve polymer chains was extracted by Soxhlet extraction to obtain pure polymer materials. Alternatively, other research teams have mixed (native and chemically modified) agarose with various IL (protic and aprotic) to build flexible solid electrolytes suitable for supercapacitors (Kim et al., 2015; Trivedi, Bhattacharjya, Yu, & Kumar, 2015; Trivedi, Srivastava, Rogers, & Kumar, 2012). Gelatin (Leones et al., 2012; Vidinha et al., 2008) and chitosan (Dias et al., 2013; Jia et al., 2014) were also exploited with ionic liquid. Chemical ionogels including cellulose (Buchtová, Guyomard-Lack, & Le Bideau, 2014; Matsumi et al., 2009) and crosslinked chitosan (Guyomard-Lack, Buchtová, Humbert, & Le Bideau, 2015) have been reported.

In view of building robust and performant biohybrid ionogels, guar gum constitutes a promising candidate as polymer matrix. Guar gum is a galactomannan constituted of a β-1,4 mannose backbone bearing α-1,6 galactose moieties randomly distributed in C-6 position with interesting attributes linked to its natural origin (extracted from seeds of leguminous shrub Cymopopsis tetragonolobus), a semi-rigid character and an aptitude to impart viscoelasticity in solvent medium. Aiming at designing sustainable polysaccharide-containing ionogels, guar gum constitutes a highly relevant building-block, advantageously distinguishable from other polysaccharides due to its moderate hydrophilicity (only dispersable in water and not totally soluble), its high thermal stability (guar gum is used for assisted oil recovery (Cheng & Prud’homme, 2000; Prud’homme, Constien, & Knoll, 1989)) and the commercial availability of very high molecular weights (up to 20000 KDa). Recently, we have demonstrated that guar gum strongly interacts with imidazolium-based ILS and that butylmethylimidazolium chloride (BMIMCl)/guar gum binary compositions lead to the formation of ionogels with relevant elastic properties (Lacroix, Sultan, Fleury, & Charlot, 2012; Verger et al., 2014). However, the scope of this first generation of ionogel was hampered by the progressive leakage of BMIMCl over time and high guar gum molecular weights were required to get good properties, which may impair the quality of the guar gum chain dissolution in IL medium and limit the processability of the materials. In this context, we anticipated that incorporation of an additional macromolecular component (such as poly(ionic liquids) (Yuan, Mecerreyes, & Antonietti, 2013)), chosen so that strong synergistic interactions can be established with both guar gum and IL, could not only favor mechanical reinforcement of the resulting ionogels but also improve dimensional stability and processability without altering the properties of conductivity. Herein, we report on the straightforward and efficient formation of three-component ionogels as bulk materials or self-standing films which integrate the rational use of (i) guar gum, (ii) BMIMCl and (iii) imidazolium-based poly(ionic liquid) (PIL) (poly-(1-[2-acryloylolethyl]-3-methylimidazolium bromide) (PAEMIBr)) (Zhang et al., 2015) (Fig. 1).

We demonstrate that highly conductive and elastic ionogels can be easily prepared through the simple addition of guar gum in PIL/IL solution, by using rheological dynamic measurements, thermogravimetric analysis, broadband dielectric spectroscopy and small and wide angle X-ray scattering measurements.

2. Experimental

2.1. Materials

Guar gums from seeds of Cymopopsis tetragonolobus (with $M_w = 58$ kg/mol and 566 kg/mol referenced as Guar58K and Guar56K) were complimentarily provided by Solvay (France). The mannose/galactose (M/G) ratio was found to be equal to 1.33 as determined by $^1$H NMR spectroscopy. Guar gum was dried before use (90°C under vacuum overnight). 1-butyl-3-methylimidazolium chloride (BMIMCl) (>97%) mp 75°C was purchased from Aldrich and dried (80°C under vacuum overnight) before use. BMIMCl will be denoted as IL (for ionic liquid) in the following of the manuscript. The synthesis of the imidazolium acrylate-based ionic liquid (1-[2-acryloylolethyl]-3-methylimidazolium bromide: AEMIBr) as well as its RAFT polymerization have been described elsewhere (Zhang et al., 2015).

The notation PIL corresponds to poly(AEMIBr) having a molecular weight close to 100 000 g/mol. A summary of the experimental conditions and the final features of the resulting PIL are gathered in Table S1. The Tg (middle point) value of PIL evaluated from DSC analyses is 65°C.

2.2. Biobroad material preparation

2.2.1. Typical procedure for the preparation of a guar/PIL/IL ternary blend

An appropriate weight amount of dried PIL was added to dried BMIMCl under stirring with a magnetic stirrer, for 12 h under inert atmosphere (nitrogen or argon) at 80°C. Then, an appropriate weight amount of dried guar gum (powder) was progressively added to the PIL/IL solution and the resulting blend was continuously stirred under inert atmosphere for 12h at 80°C. Concentrations in weight percent (wt.%) of PIL were varied depending on the analysis to be performed. The resulting samples were macroscopically transparent. Each sample was stored under dry N₂ atmosphere to avoid water uptake.

In the following of this article, the sample nomenclature will be further defined as Guarₐ (%)/PILxB%)/IL or PIL (B%)/IL, where a corresponds to the molecular weight of guar gum and A and B the weight concentrations of guar gum and PIL, respectively.

2.2.2. Guar/PIL/IL films

The films were prepared by casting guar/PIL/IL gel between two glass sides which were manually pressed. The blend was cooled down at 4°C for three days and finally recovered as a free-standing film (with a thickness around 2.5 mm as determined by a mechanical sensor). It was then subjected to washings with ethanol (15s of exposure to ethanol jets) to expel IL molecules, which are not strongly embedded in the network. The films were further dried at 60°C overnight.

2.3. Characterization

2.3.1. Rheological measurements

The viscosity ($η$) of all samples was measured by using a controlled-stress rheometer (DHR2, TA instruments Inc., UK) with an aluminum plate geometry (diameter 40 mm, gap 500 μm). The overlap concentration ($C^*$) was determined from the logarithmic evolution of $η$ at the Newtonian plateau ($η_{Newtonian}$) (at a shear rate $= 1 s^{-1}$) as a function of the polymer weight concentration. We considered $C^*$ as the concentration for which $η_{Newtonian}$ deviates from the linearity (Gericke, Schlufter, Liebent, Heinze, & Budtova, 2009; Kuang, Zhao, Niu, Zhang, & Wang, 2008; Sesouasse, Le, Ries, & Budtova, 2010). A detailed typical illustration is given in Fig. S1.
Dynamic viscoelastic properties were determined with the same rheometer using a cone/plate geometry (diameter 40 mm, angle 1:59:38 deg:min:sec). All dynamic rheological data were checked as a function of strain amplitude to ensure that the measurements were performed in the linear domain. Typically, the applied strain during the dynamical measurements was settled at 1% for PIL/IL and 0.1% for guar/PIL/IL ternary blends. The temperature was precisely controlled by a Peltier system. A particular care was taken in order to prevent the moisture uptake during measurements by using a homemade cover. The rheological properties were shown to be reproducible and stable on the time scale of the experiment (Fig. S2 and Fig. S3). The time-dependent recovery of elastic modulus $G'$ was recorded during deformation (strain 1%, linear viscoelastic region) for 100 s at a frequency of 15 Hz followed by a deformation of the gel (employing strain at 55%, outside linear viscoelastic regime) for 300 s at a frequency of 15 Hz. The cycle was repeated 8 times. The $G'$ recovery was monitored during the entire deformation-restoration process.

2.4. Thermogravimetric analysis

TGA measurements were performed under nitrogen using a TA Instruments TGA Q500 apparatus at a heating rate of 10 °C/min.

2.5. Infrared analysis

FTIR spectra were recorded using KBr pellets with a Magna-IR Nicolet 550 collecting 32 scans from 500 to 4000 cm$^{-1}$. KBr pellets for solid samples were prepared by grinding the sample with solid potassium bromide (KBr) and applying pressure (10 t) for 10 min to the dry mixture.

2.6. Cryo-SEM analysis

The sample was inserted in a sample holder at room temperature, delicately introduced in a Gatan Alto 2500 cryo-chamber and slowly cooled down to −150 °C. Then, it was fractured with a cold blade and a platinum coating was applied to increase the surface
conductivity. The sample was then introduced into the microscope chamber where the temperature was maintained at −150 °C during the analysis. Samples were observed on a FEI Quanta 250 scanning electron microscope at an accelerating voltage of 10 kV. The energy-dispersive X-ray (EDX) spectroscopy analysis was collected on various 5 μm × 5 μm zones at −150 °C.

2.7. X-ray scattering analysis

Small and wide angle X-ray scattering (SAXS and WAXS) measurements were performed at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on BM02-D2AM beamline. Depending on their viscosity, the samples were either placed in capped glass tubes (internal diameter of 2.6 mm, wall thickness of 0.2 mm, from Deutero GmbH, ref. 29604 15) or between 250 μm Kapton foils stuck on 1.6-mm-thick washers. Measurements were performed on samples equilibrated at either 25 °C or 80 °C. The incident photon energy E was set to 17.000 keV (ΔE/E = 10−4) to limit attenuation by the glass tubes. The sample-to-detector distance was D = 1.57 m, leading to a q-range from 10−2 to 2.3 10−1 Å−1 in the SAXS configuration and D ≈ 10 cm was used in the WAXS configuration for a q-range from 0.22 to 3 Å−1. The two-dimensional data were corrected for camera distortion, dark image reading and flat field response of the detector. The position of the direct beam was determined with attenuators and the calibration was performed thanks to a silver behenate standard. The corrected two-dimensional data were averaged azimuthally to obtain intensity vs scattering vector q (q = (4π/λ)sin(θ), where 2θ is the scattering angle and λ is the incident wavelength). Finally, the scattering data were corrected for the scattering from the empty cell (glass tube or Kapton windows) and normalized by the thickness and attenuation of the samples. For SAXS data treatment, the contribution from the solvent (BMIMCl) was not subtracted: when brominated PIL is dissolved at high concentration, bromide can be exchanged with chloride from the IL and the solvent contribution depends on Br-PIL concentration. For this reason, a flat contribution from the solvent Isol (experimentally increasing with Br− concentration in the concentration range of our study) was taken into account when modeling the SAXS data. For semi-dilute (C > Cc) polymer solutions of PIL or guar gum, we used a Lorentzian function to fit the SAXS data:

\[ I(q) = I_0/(1 + \xi^2 q^2) + I_{\text{sol}}, \]

where \( \xi \) is the correlation length of concentration fluctuations and \( (I_0 + I_{\text{sol}}) \) is the scattered intensity extrapolated at \( q = 0 \).

As the ternary blend contains a water uptake of around 3% (see TGA analysis in Fig. S4), the impact of a drying step (80 °C, overnight) on the internal organization was assessed (Fig. S5). The scattering profile at 25 °C is barely modified indicating that water naturally present into GuarSSK (5%)/PIL (10%)/IL does not induce any additional internal structuration in the q-range of the experiment.

2.8. Ionic conductivity measurements

Ionic conductivity was measured using a high-resolution Alpha-Analyzer (Novocontrol GmbH) assisted by a Quatro temperature controller. The samples were prepared by placing the material under study between two freshly polished platinum electrodes. The thickness of the sample cell was controlled by employing 1 mm thick Teflon spacers. Frequency sweeps were performed isothermally from 10 MHz to 0.1 Hz by applying a sinusoidal voltage of 0.1 V over a range of temperature from 30 °C to −60 °C or from 140 °C to −60 °C in steps of 10 °C. The ionic conductivity of the materials under investigation, corresponding to direct current conductivity \( (\sigma_{DC}) \) of the samples, is determined by definition from the value of the plateau observed in the frequency dependence of \( \sigma \). The plateau corresponds to the spectral region where the electrical response is dominated by the long-range diffusion of the ionic species (Sangoro, Iacob, Serghie, Friedrich, & Kremer, 2009; Serghie, Tress, & Kremer, 2009). The measurements were carried-out before and after thermal treatments performed in the cryostat of the dielectric spectrometer under a flow of pure nitrogen. The optimal drying step consisted in a thermal treatment of 6 h at 140 °C under nitrogen flow, thus excluding the presence of oxygen and humidity in the measurement chamber. After completing the measurements, the conductivity values were re-measured to ensure stable and reproducible experimental results. The reproducibility was additionally verified by measuring conductive properties on two different samples made of the same components with similar compositions.

3. Results and discussion

3.1. Material preparation and rheological characterization

The three-component Guar/PIL/IL material was prepared according a straightforward and non-degrading pathway requiring no chemical derivatization (Fig. 1). Poly(1-[2-acryloyloxyethyl]-3-methylimidazolium bromide: AEMBr) chains (2) with Mn ∼ 100 000 g/mol (see details in experimental part) (Zhang et al., 2015) were first introduced in dried BMIMCl (1). The similarity in terms of chemical structure and polar character of PIL(AEMBr) and BMIMCl (namely hydrophilic imidazolium derivatives with halogen counterion) explains the good solvating capability of this IL type for PIL chains, as macroscopically reflected by the formation of a transparent solution (see top picture in Fig. 1). Dried guar gum (3) (at 5 wt.%) was then added into the PIL/IL solution at 80 °C to give the corresponding ternary Guar/PIL/IL blend. After cooling down at room temperature, GuarSSK (5%)/PIL (10%)/IL blends appears as optically transparent materials with a macroscopic solid-like behavior, which can be easily shaped by casting onto glass plates to afford free-standing, flexible films (picture in Fig. 1). The structure and the properties of the ternary blends (as bulk materials and not films) were further in-depth investigated. Fig. 2 displays the evolution of the dynamic shear measurements of the ternary blend GuarSSK (5%)/PIL (10%)/IL, compared to PIL (10%)/IL solution. Note that the used concentrations of guar gum and PIL chains (5 and 10% respectively) are higher than their corresponding overlap concentration Cc (experimentally found to be 1.8 wt.% and 0.5 wt.% for
Guar58K and PIL100K in BMIMCl, respectively, see an example in Fig. S1.

From Fig. 2, it can be seen that the rheological response of the PIL (10%)/IL binary blend is typical of a polymer solution with a viscously dominated behavior. The viscosity is mainly brought by the formation of PIL chain topologic entanglements (as C ∗ C∗) in addition to favorable PIL/PIL and PIL/IL physical interactions. Indeed, as reported in literature, in alkylimidazolium halides-based ionic liquid (as the ones used in this work), cations and anions can connect each other not only via electrostatic interactions but also through hydrogen bonds (one halide counter-anion is able to develop hydrogen bonds with acidic protons of the imidazolium ring) (Heinze et al., 2008). More interestingly, from Fig. 2, it can be seen that the incorporation of guar gum (at 5 wt.%) into the PIL/IL viscous solution considerably changes the rheological properties. G′ exceeds G″ in the measured linear range of frequency with a G′ value reaching 6000 Pa at 10 Hz against 200 Pa and 300 Pa for Guar58K (5%)/BMIMCl (data not shown) and PIL(10%)/IL, respectively. The ternary blend presents an elastic dominated behavior, which is consistent with the macroscopically observed solid state (see picture in Fig. 1). The addition of Guar58K at only 5 wt.% induces a remarkable G′ modulus enhancement by playing a role of mechanical reinforcing agent when it is combined with PIL chains. It is important to mention that this route to solid-like behavior exclusively requires two successive dissolution steps and does not rely on the use of complex macromolecular architectures. In this ternary blend, synergistic interactions are developed between guar and P(AEMIBr) chains as well as between BMIMCl molecules. Interactions within the ionogel were investigated by infrared (FTIR) spectroscopy (see FTIR spectra of dried guar gum and Guar58K(5%)/PIL(10%)/IL, given in Fig. 3). A shift of the absorbance peak corresponding to the hydroxyl stretching band of guar gum is observed after the incorporation of IL and PIL chains. As it was reported, this means that the O–H bond strenght increases (Ohno, Shimoaka, Akai, & Katsumoto, 2008) which reflects the establishment of interactions between guar gum chains, PIL and IL mediated by hydrogen bonding. In literature, such shift of the OH absorbance has been ascribed to the formation of hydrogen bonds between guar gum (Lacroix et al., 2012) or poly(vinyl alcohol) (Yoon, Lee, & Stafford, 2011) and ionic liquids containing halide as counter anion. The team of Rogers has also evoked the formation of hydrogen bonds between hydroxyl functions of cellulose and the anions of the ionic liquid, which explains its good dissolution ability (Swatloski, Spear, Holbrey, & Rogers, 2002; Moulthro,

Swatloski, Moyna, & Rogers, 2005). From these earlier studies, we can assume that hydrogen bonds are developed between the electronegative halide anion belonging both to BMIMCl and P(AEMIBr) and the −OH groups of guar gum. Moreover, the acidic protons of the cation at C2 and C4 position of the imidazolium ring of BMIMCl and P(AEMIBr) can be involved in hydrogen bonds established with −OH groups of guar gum.

Moreover, Coulombic interactions between charged moieties (PIL/IL and IL/IL) favorably contribute to the observed increase of G′ and G″ moduli. Furthermore, given the used chain concentrations (C ∗ C∗), one can assume that guar/guar, PIL/PIL and especially guar/gum/PIL chain entanglements are also contributing to the elasticity enhancement. All these interactions result in the construction of a mixed network. Nevertheless, the non-covalent nature of the interactions implies a G′ and G″ dependence with frequency, which highlights the transient character of the network and the overall relaxation of the system with time. No macroscopic heterogeneity is detected within the material. Indeed, the crystallization of BMIMCl is hampered owing to favorable interactions with guar gum and PIL chains.

To gain insights into the impact of the Guar58K(5%)/PIL/IL composition on the rheological behavior, ternary blends with PIL concentrations (C_PIL) ranging from 5 to 20 wt. % were subsequently investigated (Fig. 4).

Up to a PIL concentration of 5 wt.%, G′ is greater than G″ on the entire detected frequency range indicating that the ternary blend exhibits a viscoelastic fluid-like state with a rheological behavior dominated by viscous effects. G′ scales approximately with frequency (f) as G′ ∼ f^0.78, which deviates from the terminal relaxation regime of G′ ∼ f^2 expected for classical polymer solutions. This slope deviation can be ascribed to the existence of interchain guar gum/PIL interactions, which are magnified with PIL concentration. At a 8 wt.% PIL concentration, G′ and G″ moduli are of similar magnitudes and follow relatively close frequency dependence (G′ ∼ G″ ∼ f^0.44), which is typical of a transition between liquid-like and solid-like behavior and closely approximates the gel point. When the PIL concentration increases, the response exhibits a clear elastic behavior and the terminal cross-over point, which is related to the intra and inter-forces and to the longest relaxation time τd (Mours & Winter, 1996; Soltero, Puig, & Manero, 1996) is no more visible in the frequency experimental window. At a PIL concentration of 20 wt.%, the ternary blend behaves as a physical ionogel with almost no variation of both moduli with frequency over the entire measured range. G′ is significantly larger

![Fig. 3](image1.png) FT-IR spectra of the hydroxyl vibration region for guar gum (a) and guar (5%/PIL10%/BMIMCl) (b); All samples were carefully dried (80 °C under vacuum for 2 days) before IR analysis.

![Fig. 4](image2.png) Frequency-dependence of G′ (filled symbols) and G″ (open symbols) moduli of Guar58K (5%)/PIL/IL, with a PIL concentration equals to 5% (♦), 8% (♦), 10% (♦) and 20% (♦) at 25 °C.
than $G''$ and reaches 30,000 Pa. This ionogel (Guar$_{58K}$ (5%)/PIL (20%)/IL) presents outstanding elastic properties, and to the best of our knowledge, such values of shear $G'$ modulus have never been reported for polysaccharide-containing physical ionogels (Sharma, Mondal, Mukesh, & Prasad, 2013; Trivedi et al., 2012, 2015), which again emphasizes the key role of guar gum when it is associated to PIL chains. We can reasonably assume that guar gum possesses a chain conformation particularly adapted to develop favourable interactions with P(AEIMBr) chains. A similar elasticity enhancement was observed for ternary blend containing PIL and guar gum with higher molecular weight (566 kg/mol) (Fig. S6). We further quantified the influence of temperature on viscoelastic moduli (up to 60°C). A temperature increase leads to a decrease of $G'$ and $G''$ as well as a shortening of the longest relaxation time, while maintaining a $G'$ value higher than $G''$. A time-temperature superimposition (TTS) was successfully applied to the guar/PIL/IL blends and master plots of storage and loss modulus were built (Fig. S7). A horizontal shift factor $a_s$ was applied and its dependence with temperature has been described by the Arrhenius (Caputo, Selb, & Candau, 2004; Sammons, Collier, Rials, & Petrovan, 2008) equation over the 10–60°C temperature range, which allows us for determining the apparent activation energy ($E_a$) value (at $T = T_{ref}$, i.e. 25°C) close to 105 kg/mol. Similar Arrhenius behavior was reported for cellulose/BMIMCl solutions (Ahn et al., 2016). This high $E_a$ value can be attributed to the high viscosity of BMIMCl, but also to the establishment of polar interactions between the three components (mainly hydrogen bonds) and entanglements between all polymer chains. To highlight the propensity of the gel to be reversibly reorganized, the elastic recovery of Guar$_{58K}$ (5%)/PIL (10%)/IL upon relaxation was further investigated (Fig. 5).

The material was first subjected to 1% strain (linear regime) for 300 s and $G'$ was monitored during the process followed by strongly deforming the gel employing high strain (at 15 Hz for 100 s). Guar$_{58K}$ (5%)/PIL (10%)/IL ionogel exhibited a very rapid and total recovery in its elasticity behavior after a breakdown at oscillations of a large amplitude, as a result of the non-covalent and dynamic character of the interactions. The recovery was fully reproducible for at least seven successive deformation-relaxation cycles. This ternary blend can be thus reversibly deformed and displays a relevant linear/non linear recovery behavior, which may be very advantageous for developing materials with shape-memory behavior. A similar recovery was reported by Nagasawa et al. (2012) for oligomeric electrolytes and ionogels, and was ascribed to the presence of long-range electrostatic interactions (Nagasawa, Matsumoto, & Yoshida, 2012; Yoshida et al., 2007). Sharma et al. also described comparable reversible behavior for guar gum/BMIMCl gels containing multiwalled carbon nanotubes or tamarind gum-based soft ionogels (Sharma, Mondal, Mukesh, & Prasad, 2014). However, $G'$ recovery was not instantaneous for these materials.

### 3.2. Thermal and dimensional stability of Guar/PIL/IL ternary blends

Thermogravimetric analysis revealed that the thermal stability of ternary blend is substantially improved compared to native guar gum (Fig. S4) (observed at 310°C and 260°C, respectively). TGA analysis also showed that the water uptake within the ternary blend is around 3.3 wt.% (after a storage of 1 week at room temperature under ambient conditions).

As previously mentioned, the dimensional stability and the absence of IL exudation are key points in view of generating polymer electrolytes. Guar$_{58K}$ (5%)/PIL (10%)/IL as bulk materials or free-standing films were introduced in an oven at 50°C and the exudation of IL from the material was macroscopically monitored for 1 month. As shown in Fig. 6, no IL leakage was observed and both materials maintain their initial size and shape. This structural stability confirms an efficient confinement of IL molecules within the materials, even at 50°C. It should be noted that room temperature stable thin films prepared from the ion gel of guar gum and BmimCl by the application of high pressure was reported (Mine, Prasad, Izawa, Sonoda, & Kadokawa, 2010; Prasad, Izawa, Kaneko, & Kadokawa, 2009). Films thus obtained showed to have high temperature shape-able behaviour and were highly conducive in nature.

### 3.3. Nanostructure of Guar/PIL/IL ternary blends

Synchrotron X-ray scattering techniques such as WAXS and SAXS measurements were further performed to obtain structural information on the samples as well as pure IL. The WAXS profile of the Guar$_{58K}$ (5%)/PIL (10%)/IL ionogel was compared to BMIMCl (previously molten and kept under a thermodynamically stable liquid at room temperature) (Fig. S8). The WAXS pattern of BMIMCl displays a typical amorphous halo with only a small shoulder at $q^* = 1.05\AA^{-1}$. Indeed, such a short-chained imidazolium ionic liquid is not expected to self-assemble at the molecular scale into ordered micellar/lamellar structures as long-chain surfactants (Bradley et al., 2002; Katayanagi, Hayashi, Hamaguchi, & Nishikawa, 2004; Triolo, Russina, Bleif, & Cola, 2007). The shoulder is ascribed to the ordering resulting from physical interactions, such as Coulombic interactions between anions and cations, and hydrogen bonds between the chloride anion and the proton in C2 position of the imidazolium ring (Saha, Hayashi, Kobayashi, & Hamaguchi, 2003; Triolo et al., 2007). The WAXS pattern (I vs. q) of the ternary blend stays similar to the one of BMIMCl. Indeed, no diffraction peak is observed and the scattering profile is dominated by the response of BMIMCl, which indicates that the Guar$_{58K}$ (5%)/PIL (10%)/IL is exempt of crystalline domains and the morphology of the solvent is not altered by the addition of the polymers. To get deeper insight into the structure of the different blends, SAXS measurements (I vs. q) were further recorded on PIL (10%)/IL and Guar$_{58K}$ (5%)/PIL (10%)/IL at 20°C (Fig. 7). For comparison, the SAXS pattern of BMIMCl is also included.

The pattern of the IL amorphous solvent is flat in the SAXS q-range (i.e. from 1.10$^{-2}$ to 2.3 10$^{-1}$ Å$^{-1}$). Furthermore, the scattering profiles and the observed slopes for PIL/IL and Guar/PIL/IL samples suggest the absence of well-defined chain aggregates detectable...
in the q-range of our scattering experiments (Fig. 7: curves b and c). The scattered intensity of the PIL(10%)/IL solution is relatively weak, possibly due to the poor electronic contrast between PIL and IL, due to their chemical similarity and ion exchange (Br⁻ vs Cl⁻) between the PIL and the IL. The I vs. q profiles of PIL(10%)/IL were fitted with the Lorentzian function equation classically (in dotted line in Fig. 7) used for semi-dilute polymer solutions (see Experimental part) (Hamada, Kinugasa, Hayashi, & Nakajima, 1985; Saito & Hashimoto, 2002). The resulting correlation length l for the PIL58K (10%)/IL solution is of the order of 37 Å, which is probably low due to the high PIL molecular weight, together with a chain concentration (10 wt.%) well above C* (0.5 wt.%). The scattered intensity from the Guar58K/5%)/PIL(10%)/IL ternary blend is much higher (Fig. 7: curve c), suggesting the presence of intermolecular interactions implying guar gum/PIL associations (interactions and entanglements), which is consistent with the FTIR analysis and physical gel-like behavior (see rheological properties vide supra), contrary to the viscously dominated behavior of PIL (10%)/IL solutions. Moreover, in the low q-range region the scattering profile of the ternary blend displays a slope lower than -2; as a consequence, the experimental data cannot be fitted anymore with a Lorentzian function (or a sum of Lorentzian functions) (as shown in Fig. 7). Complementarily to WAXS/SAXS analyses, Cryo-SEM experiments collected on a cross section of the ternary blend revealed homogeneous and uniform structure: no large aggregated/segregated regions are visible at the micrometric scale (Fig. S9). Also, EDX analysis (data not shown) recorded for different regions of the Guar58K(5%)/PIL(10%)/IL sample indicated an homogeneous partition (in the micron-range) of bromide, chloride, carbon, nitrogen and oxygen elements within all samples.

3.4. Ion transport properties

From an application point of view in the energy field, an important property of polymer electrolytes is the ionic conductivity (σ).² The ionic conductivity was determined by broadband dielectric spectroscopy. As a typical example, Fig. S10 shows the frequency dependence of the conductivity σ' (σ' = ϵ'ε'ε₀, where ε₀ is the vacuum permittivity and ϵ' is the dielectric loss) of the ternary blend under isothermal conditions for temperatures ranging from 30°C to ~90°C before thermal pretreatment. To ensure a quantitative removal of adsorbed water within the hygroscopic material a heat treatment (at 140°C for 6 h) was applied. Indeed, water molecules can promote the ion dissociation and the ionic transport, leading to higher conductivity of electrolytes (Akgol et al., 2007; Spohr & Patey, 2010). The resulting σ_Dc of the Guar58K(5%)/PIL(10%)/IL ternary blend (before and after thermal treatment) was plotted as a function of inverse temperature (Fig. 8).
As commonly observed, the conductivity increases with temperature as their viscosity decreases and mobility is greatly promoted (Sood, Zhang, Serghie, Bernard, & Drockenmuller, 2015). Moreover, from Fig. 8, the temperature-dependence of the conductivity exhibits the same convex upward curved profiles over the entire temperature range, well described by the Vogel-Fulcher-Tammann (VFT) equation: \( \sigma_{\text{DC}} = \sigma_0 \exp(-B/T-T_0) \), where \( \sigma_0 \) is the ionic conductivity at infinite temperature, \( B \) a fitting parameter related to the activation energy of ion conduction, and \( T_0 \), the Vogel temperature linked to the ideal glass temperature (Buchtová et al., 2014; Dias et al., 2013; Trivedi et al., 2012; Vidinha et al., 2008). Fig. 8 underpins that the Guat58%(5%)/PIL(10%)/IL ternary blend (before the drying step) exhibits high conductive properties with a \( \sigma_{\text{DC}} \) value of 7.5 \( \times 10^{-5} \) cm\(^{-1} \) at 30°C (compared to 1 \( \times 10^{-3} \) S cm\(^{-1} \) for PIL(10%)/IL data not shown). In spite of the presence of strong PIL/Guar gum interchain interactions leading to gel-like behavior with high \( G' \) moduli (6000 Pa), the ion mobility is sufficient enough to lead to high conductivity. This conductivity level demonstrates that ionic conductive paths are formed in the ionogel matrix. The presence of a high amount of free IL molecules also contributes to the high conductivity of the resulting materials. The conductivity values are of the same order of magnitude (ranging from 10\(^{-3}\) to 10\(^{-1}\) S/cm) as the ones reported in the literature for polysaccharide-based ionogels (Buchtová et al., 2014; Dias et al., 2013; Guyomard-Lack et al., 2015; Huang et al., 2008; Jia et al., 2014; Leones et al., 2012; Liang et al., 2015; Matsumi et al., 2009; Ramesh, Shanti, & Morris, 2013; Vidinha et al., 2008). Comparisons remain difficult, as conductivity and mechanical properties need to be rigorously balanced and the mechanical properties were scarcely described in the papers mentioned above. Under anhydrous conditions, the conductivity drops to 5.5 \( \times 10^{-5} \) S cm\(^{-1} \) at 30°C, which remains significantly high. The values obtained from the best fittings of the experimental curves are given in Table S2. The B parameter, linked to the activation energy for ionic transport, is notably higher before the thermal treatment, possibly due to the presence of water which modifies the mobility. Thus, this ternary blend meets all the requirements of a solid polymer electrolyte since it combines high elastic modulus, a relevant dimensional stability (without ionic liquid leakage), a good thermal stability (up to 310°C) with a high conductivity.

### 4. Conclusion

In summary, we developed a straightforward and robust route to high-performance ionogels, based on the simple addition of guar gum in a solution of poly(1-[2-acryloyloxyethyl]-3-methylimidazolium bromide) in BMIMCl at 80°C. The viscoelastic response emphasized the formation of solid-like material, whose rheological properties can be precisely adjusted by varying the PIL weight concentration. High energy activation value was determined and ionogels with high elastic modulus (up to 30,000 Pa) were successfully designed. Guar gum chains act as gelators once associated with PIL chains in the IL medium. Polar interactions (mainly hydrogen bonds) between guar gum and PIL chains as well as chain entanglements are responsible for the formation of the materials. Moreover, the resulting materials are thermally stable (up to 310°C) and dimensionally stable (with no IL leakage with time). WAXS and SAXS measurements revealed that even though interchain interactions are formed between the constituents of the ternary blend, no (nano)phase separation or well-defined chain aggregates are observed. Interestingly, the ionogels exhibit high conductive properties (superior to 10\(^{-4}\) S/cm at 30°C), as the result of homogeneous distribution of IL molecules within the materials. These multicomponent materials offer durable high-performance to be considered as polymer electrolytes while respecting sustainabilility, for instance as gel electrolyte for biobattery systems and supercapacitors.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [http://dx.doi.org/10.1016/j.carbpol.2016.10.050](http://dx.doi.org/10.1016/j.carbpol.2016.10.050).

### Complementary rheological, thermal, morphological analysis and conductive properties.

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