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# New polymer electrolyte membrane for medium-temperature fuel cell applications based on cross-linked polyimide Matrimid and hydrophobic protic ionic liquid

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## A B S T R A C T

New hydrophobic protic ionic liquid, 2-butylaminoimidazolium bis(trifluoromethylsulfonyl)imide (BAIM-TFSI), has been synthesized. The ionic liquid showed good thermal stability to at least 350 °C. The conductivity of BAIM-TFSI determined by electrochemical impedance method was found to be  $5.6 \times 10^{-2}$  S/cm at 140 °C. Homogeneous composite films based on commercial polyimide (PI) Matrimid and BAIM-TFSI containing 30–60 wt% of ionic liquid were prepared by casting from methylene chloride solutions. Thermogravimetric analysis data indicated an excellent thermal stability of PI/BAIM-TFSI composites and thermal degradation points in the temperature range 377 °C–397 °C. The addition of ionic liquid up to 50 wt% in PI films does not lead to any significant deterioration of the tensile strength of the polymer. The dynamic mechanical analysis results indicated both an increase of storage modulus  $E'$  of PI/BAIM-TFSI composites at room temperature and a significant  $E'$  decrease with temperature compared with the neat polymer. The cross-linking of the PI with polyetheramine Jeffamine D-400 allowed to prepare PI/Jeffamine/BAIM-TFSI (50%) membrane with  $E'$  value of 300 MPa at 130 °C. The ionic conductivity of this cross-linked composite membrane reached the level of  $10^{-2}$  S/cm at 130 °C, suggesting, therefore, its potential use in medium-temperature fuel cells operating in water-free conditions.

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## 1. Introduction

Polymer electrolyte membrane fuel cells are considered as promising alternative energy sources for stationary, automotive, and portable applications because of their high efficiency in converting chemical energy stored in hydrogen fuel directly into electrical energy, with water being the only by-product. The main functions of polymer electrolyte membrane or proton exchange

membrane (PEM) are to avoid direct contact between fuel and air as well as to ensure efficient proton transfer from the anode to cathode side [1]. Low-temperature PEM fuel cells working at about 80 °C with perfluorosulfonic acid ionomers (e.g., Nafion) as electrolyte have been widely used for a long time. In the hydrated state, Nafion membranes have excellent proton conductivity because of the formation of continuous ion-conducting clusters by both sulfonic groups and water molecules [2]. However, the high-temperature PEM fuel cells operating in the temperature range of 120 °C–200 °C are more promising because of their significant advantages, such as increased tolerance to catalyst poisoning by carbon dioxide, enhanced electrode kinetics, easier heat

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dissipation, and water management [3,4]. Under such conditions, Nafion membranes lose their conductivity because of water evaporation [4].

Polybenzimidazole (PBI) impregnated with phosphoric acid is commercially available proton-conducting system, which provides good level of proton conductivity above 100 °C without external humidification [3,5,6]. In PBI matrix, H<sup>+</sup> ions can migrate through the polymer backbone by means of hydrogen bonds, assisted by phosphate anions [3,5]. However, PBI/H<sub>3</sub>PO<sub>4</sub> membranes have such drawbacks as partial loss of phosphoric acid (that leads to reduced proton conductivity) when the operating temperature of the fuel cells is below 100 °C [5,6]. It should also be noted that the cost of both Nafion and PBI-based PEMs remains still high.

During the last decades, various approaches have been proposed to develop alternative PEM for high-temperature fuel cell applications at reasonable cost. Thus, sulfonated poly(ether ether ketone) (SPEEK) as well as other sulfonated rigid aromatic polymers, such as polyphenylsulfone, polyethersulfone, and polyimides (PIs), were studied as possible alternative ionomers [3,6–11]. Both organic and inorganic solid proton-conducting electrolytes have also been developed for water replacement in PEM, such as imidazole derivatives [8], heteropolyacids [9], zirconium phosphate [10], and polyaniline [11–13]. Composite membranes, based on zirconium phosphate or calcium phosphate and imidazolium-based aprotic ionic liquids, supported on polytetrafluoroethylene, were found to have excellent anhydrous proton conductivity at high temperature of 200 °C [14,15]. The ionic liquid component was supposed to act as a proton bridge [14].

Recently, the protic ionic liquids (PILs), which are low-temperature molten salts of Brønsted acids and Brønsted bases, have proved to be extremely promising proton-conducting electrolytes for fuel cells applications [16–20]. In contrast to aprotic ionic liquids, PILs have a mobile proton located on the cation, which can be transferred from the acid to the base, which offers intrinsic proton conductivity. The presence of proton donor and proton acceptor sites can thus be used to build a hydrogen-bonded network [16,21]. The proton conduction in PILs was found to proceed by two parallel mechanisms: diffusion and hopping (Grotthuss mechanism) [16,17]. The most studied PILs contain imidazolium, triethylammonium, diethylmethylammonium cations, and fluoro-containing anions, such as trifluoromethanesulfonate and bis(trifluoromethylsulfonyl)imide [16–19]. The ionic conductivity of PILs is commonly in a range from 10<sup>-3</sup> to 10<sup>-1</sup> S/cm both at room temperature and above 100 °C [16–18]. Moreover, these compounds possess negligible vapor pressure, high thermal stability, and nonflammability, as well as wide electrochemical window [19–21].

Composite films based on sulfonated aromatic polymers and PILs were found to be prospective alternative PEMs for high-temperature fuel cell applications. Thus, new composite membrane has been developed on the base of SPEEK and ionic liquid trifluoroacetic propylamine (TFAPA). Conductivity of 0.019 S/cm was achieved for SPEEK/TFAPA membranes containing 70 wt% of ionic liquid at 160 °C [22]. Unfortunately, these composites showed poor mechanical strength, especially at elevated temperatures. Inorganic–organic composite membranes have also been developed based on SPEEK, silica, and PIL diethylmethylammonium trifluoromethanesulfonate [dema][TfO] [23]. A proton conductivity of 0.02 S/cm was obtained for composites containing 50 wt% of ionic liquid at 220 °C. However, dynamic mechanical analysis (DMA) data indicated significant drop of storage modulus for both SPEEK/SiOx and SPEEK/SiOx/[dema][TfO] membranes above 80 °C [23].

Among many advanced polymer matrices, sulfonated aromatic PIs (SPIs) are probably one of the most promising PEMs for use in fuel cells because they combine both good film-forming properties,

excellent mechanical strength and thermal stability. Elaboration of composite membranes based on SPIs and PILs has recently been reported [24–26]. It is worth noting that the presence of sulfonic groups in PI macromolecules results in solubility in polar solvents, as well as significantly improved compatibility between polymer matrix and PIL [24,26]. Thus, SPI membranes with the ion exchange capacity of 2.27 mEq/g were found to retain four times its own weight of [dema][TfO] ionic liquid, and uniform, tough, and transparent films were obtained by solvent casting [24]. The composite membranes have good thermal stability (>300 °C) and ionic conductivity above 10<sup>-2</sup> S/cm at 120 °C under anhydrous conditions when the [dema][TfO] content is higher than 67 wt%. Deligöz and Yilmazoglu [25] reported the development of complex membranes based on SPI comprising 1-methylimidazolium cations. Although the membranes doped with sulfuric acid revealed the ionic conductivity of 5.6 × 10<sup>-2</sup> S/cm at 180 °C, they were characterized by a high hydrophilicity and poor thermal stability of conductivity because of the evaporation of adsorbed dopant. In the case of PEM based on SPI and PILs comprising TfO anion and 1-methylimidazolium or 1-vinylimidazolium cations [26], they were found to be flexible and transparent, with a good thermal stability (>350 °C) and high ionic conductivity (3–6 mS/cm) at 120 °C (at the ionic liquid content of 40–50 wt%). However, tensile strength values of SPI/PIL composites were found to be almost one order lower compared with neat SPI [26]. Successful approach has finally been reported by Pua et al. [8] when hydrophobic heterocyclic amine 2-undecylimidazole was used as an efficient proton-conducting additive. The proton conductivity of such composite reached 10<sup>-3</sup> S/cm at 180 °C.

Overall, the disadvantage of SPI is the use of toxic high boiling point solvents such as *m*-cresol or *N*-methyl-2-pyrrolidone/dimethyl sulfoxide for both polymer synthesis and film casting [24–26]. Such solvents are rather difficult to remove entirely from composite membranes and cause deterioration of composite thermomechanical properties. Moreover, the sulfonation of aromatic PI always leads to significant increase in their cost, as well as high hydrophilicity of membranes.

Accordingly, the use of nonsulfonated rigid chain polymers as a matrix for composite PEM seems very attractive from a practical point of view. However, aromatic PIs are poorly compatible with hydrophilic PILs such as [dema][TfO] [24]. To avoid this problem, the microporous support based on commercial PI Matrimid was impregnated with hydrophilic PIL, triethylammonium trifluoromethanesulfonate (TEA-TF), to obtain composite PEM with ionic liquid content up to 76 wt% [27]. At 130 °C, the membrane exhibits proton conductivity of 20 mS/cm that is very close to that of the pure PIL. In other study, Matrimid membrane with spongy, interconnected, and symmetrical porous structure was impregnated with hydrophilic PIL, 1-butylimidazolium dibutyl phosphate, by direct immersion method [28]. The composite PEM containing at least 50% v/v of ionic liquid phase showed good retention in the polymer matrix. The ionic conductivity reached the value of 2 × 10<sup>-2</sup> S/cm at 115 °C [28]. However, it should be noted that the porous polymer support, as well as its composite with PIL, had significantly reduced mechanical properties compared with dense PI films [27].

The hydrophobic PIL, 1-butylimidazolium bis(trifluoromethylsulfonyl)imide (BIM-TFSI), was found to have good compatibility with PI Matrimid [29]. Thus, due to the good solubility of Matrimid in common organic solvents, dense composite films containing up to 70 wt% of BIM-TFSI were prepared by casting from methylene chloride solution. Polyetheramine Jeffamine D-2000 was used as a cross-linking agent for PI to obtain composite membranes with satisfactory tensile strength of 18 MPa. The ionic conductivity reached 1.5 × 10<sup>-3</sup> S/cm at 180 °C that was close to the

conductivity of pure PIL [29]. Thus, the results of previous studies indicated the possibility of obtaining PEMs based on dense Matrimid PI films and PILs. The main difficulty is to choose an appropriate hydrophobic PIL, which combines high proton conductivity, thermal stability, and good compatibility with PI matrix. From this point of view, the high content of exchangeable protons in the ionic liquid structure seems to be especially important because in such a case, we can expect both high conductivity and strong physico-chemical interactions with polar carbonyl groups of PI.

Guanidinium-based ionic liquids are known to be very promising proton conductors due to the presence of six dissociable protons in guanidinium cation [30,31]. On the other hand, the high melting point of most guanidinium salts is a serious drawback for their application as proton-conducting electrolyte. Reducing symmetry of cations can reduce the melting points, and a series of room temperature PILs comprising both common and cyclic guanidinium cations and TFSI anion have been synthesized [32–34]. However, the substitution of hydrogen atoms on alkyl radicals in the guanidinium cation led to decreased proton conductivity [32,33]. New PIL based on monosubstituted guanidinium cation, N-butylguanidinium tetrafluoroborate, has been synthesized by single-step method. The ionic liquid is thermally stable to at least 300 °C and has ionic conductivity value of 0.18 S/cm at 180 °C [35]. However, N-butylguanidinium salts were found to be insoluble in low-boiling solvents like methylene chloride or tetrahydrofuran and, therefore, seem to be less attractive for the elaboration of composite membranes based on Matrimid.

In the present study, new room temperature PIL comprising cyclic guanidinium cation, 2-butylaminoimidazolium bis(trifluoromethylsulfonyl)imide (BAIM-TFSI) has been synthesized. This ionic liquid is soluble in methylene chloride, and the composite films PI/BAIM-TFSI were easily prepared by solvent casting. Moreover, because of its hydrophobic nature, BAIM-TFSI has significant advantages over common hydrophilic PILs, such as excellent compatibility with PI, as well as potential leaching resistance from PEMs during fuel cell operation. The obtained membranes were then characterized in terms of mechanical properties, thermal stability, and proton conductivity in a wide range of temperature.

## 2. Materials and methods

### 2.1. Materials

Following chemicals were used for the synthesis of ionic liquid and for the elaboration of PI-based composites: 2-imidazolidinethione, 98% (Fluka), n-butylamine, 99% (Merck), polyetheramine Jeffamine D-400 (Huntsman), lithium bis(trifluoromethylsulfonyl)imide, 99% (Acros), methanol, 98% (Sigma-Aldrich), hydrochloric acid, 37% (Sigma-Aldrich), isopropanol, 98% (Sigma-Aldrich), and methylene chloride, 99% (Sigma-Aldrich).

PI Matrimid 5218 powder was kindly supplied by Huntsman (Switzerland).

### 2.2. Synthesis of PIL BAIM-TFSI

The ionic liquid was synthesized according to the following procedure (Scheme 1).

2-Methylmercaptoimidazoline-2 chlorohydrate (MIM-HCl) was synthesized using the method described in Ref. [36]. Forty grams (0.39 mol) of 2-imidazolidinethione were suspended in the mixture of methanol (50 mL) and concentrated hydrochloric acid (50 mL) with magnetic stirrer. The mixture was heated to reflux for 12 hours. Residual methanol was distilled, and water solution was evaporated. The solid residue was then purified by recrystallization

from isopropanol. The obtained product (MIM-HCl) has melting point of 160 °C.

$^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  = 2.71 (t, 3H, CH<sub>3</sub>), 3.84 (s, 4H, CH<sub>2</sub>), 10.64 (s, 2H, NH).

The mixture of MIM-HCl (20 g, 0.13 mol), butylamine (9.5 g, 0.13 mol), and isopropanol (100 mL) was placed into a round-bottomed flask (300 mL) equipped with a reflux condenser and a magnetic stirrer. The mixture was boiled for 6 hours under constant stirring. Methyl mercaptan formed during the reaction was trapped by bubbling through the vessel contained 20% water solution of potassium hydroxide. After the reaction was completed, isopropanol was distilled at normal pressure. The liquid product of light brown color (BAIM-Cl) was dissolved in methylene chloride (50 mL), and the solution was filtered to remove nonreacted MIM-HCl. Methylene chloride was distilled off. Residual solvents were removed in vacuum 10 mbar at 70 °C for 12 hours. The yield of BAIM-Cl was 27 g (72%).

Ten grams (0.05 mol) of BAIM-Cl were dissolved in water (50 mL) under stirring, and the solution of lithium bis(trifluoromethylsulfonyl)imide (14.5 g, 0.05 mol) in 50 mL of water was added. The formed bottom layer of the ionic liquid BAIM-TFSI was extracted with methylene chloride (2 × 50 mL), washed with water (2 × 100 mL), and dried under sodium sulfate. Methylene chloride was distilled off, and residual solvent was removed in vacuum 20 mbar at 70 °C for 8 hours. The viscous liquid of light yellow color was obtained.

NMR spectra of BAIM-TFSI are shown in supplementary file.

$^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ ):  $\delta$  = 0.87 (t, 3H, CH<sub>3</sub>), 1.31 (m, 2H, CH<sub>2</sub>), 1.45 (m, 2H, CH<sub>2</sub>), 3.17 (t, 2H, NH-CH<sub>2</sub>), 3.55 (s, 4H, 4-CH<sub>2</sub>, 5-CH<sub>2</sub>), 8.1–8.8 (br s, 3H, NH).

$^{19}\text{F}$  NMR (188 MHz, DMSO- $d_6$ ):  $\delta$  = -79.92 (s, 6F, CF<sub>3</sub>).

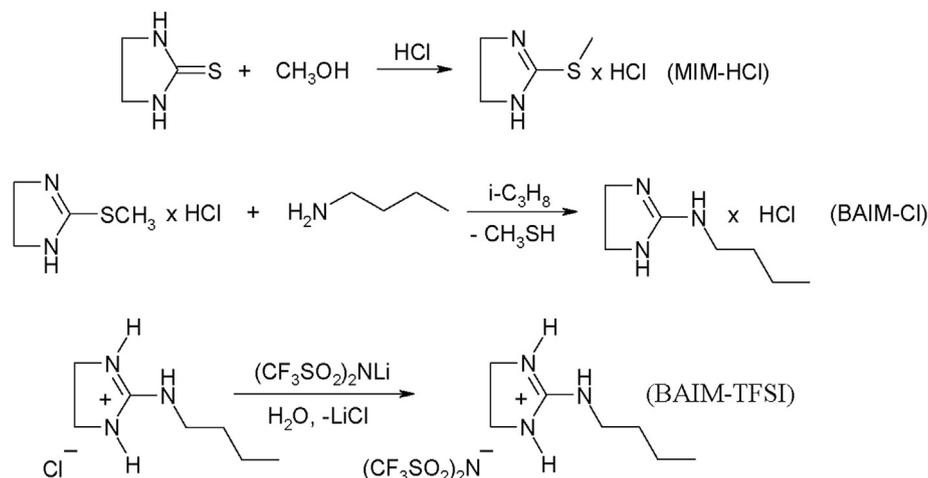
### 2.3. Elaboration of PI/BAIM-TFSI composite membranes

PI solution in methylene chloride was prepared in concentration of 5 g/100 mL. The ionic liquid BAIM-TFSI was added to the polymer solution (30–60 wt%). The obtained solution was poured onto glass support, and the solvent was allowed to evaporate at room temperature for 24 hours. Thus, transparent films with PIL content of 30, 40, 50, and 60 wt% were prepared. Residual methylene chloride was removed in vacuum 10 mbar at 60 °C for 12 hours. The thickness of membranes was 50–70  $\mu\text{m}$ .

Following method was used to prepare composite membranes based on cross-linked PI (Scheme 2) [29,37]. One gram (0.0018 mol) of PI was dissolved in 20 mL of methylene chloride followed by the addition of 5, 10, and 15 molar percent of Jeffamine D-400 with respect to PI. The solution was stirred for 24 hours at room temperature after that the corresponding amount of BAIM-TFSI was added, and the mixture was further stirred for 2 hours. Composite films PI/Jeffamine/BAIM-TFSI containing 50 wt% and 60 wt% of ionic liquid were prepared by casting the solution onto glass support. Control samples of cross-linked PI were prepared without the addition of ionic liquid. The addition of 15% of Jeffamine resulted in a high content of gel fraction, which precipitated from PI solution. Therefore, only PI samples cross-linked with 5% and 10% of Jeffamine were used for the study.

### 2.4. Characterization of PI/BAIM-TFSI composites

The vibrational properties of BAIM-TFSI and its composites with PI were studied using a Vertex-70 Bruker (Germany) Fourier Transform Infrared (FTIR) spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The spectrum of pure PIL was obtained from a tablet with KBr. PI/BAIM-TFSI composite films were placed into contact with the single reflection diamond ATR



**Scheme 1.** Synthesis of protic ionic liquid BAIM-TFSI.

(Attenuated Total Reflection) crystal, and the spectra were collected at room temperature over the range  $400\text{--}4000\text{ cm}^{-1}$  at a resolution of  $1\text{ cm}^{-1}$ .

The mechanical testing of polymer membranes was performed using P-50 universal tensile testing machine (Milaform, Russia) at a deformation rate of  $10\text{ mm/min}$ . Polymer films were cut into specimens with the size of  $35 \times 5 \times 0.02\text{ mm}$ . An average tensile strength value was calculated from tensile strength of three individual samples. DMA investigations were carried out on a dynamic mechanical analyzer Q 800 (TA Instruments) in the tension mode at frequency of  $10\text{ Hz}$  and a heating rate of  $2.0\text{ }^\circ\text{C/min}$ . The samples for DMA study were cut from Matrimid/BAIM-TFSI composite films and had the size of  $12.75 \times 4 \times 0.2\text{ mm}$ . The viscoelastic properties, mechanical loss factor ( $\tan \delta$ ) and storage modulus ( $E'$ ), were recorded as a function of temperature.

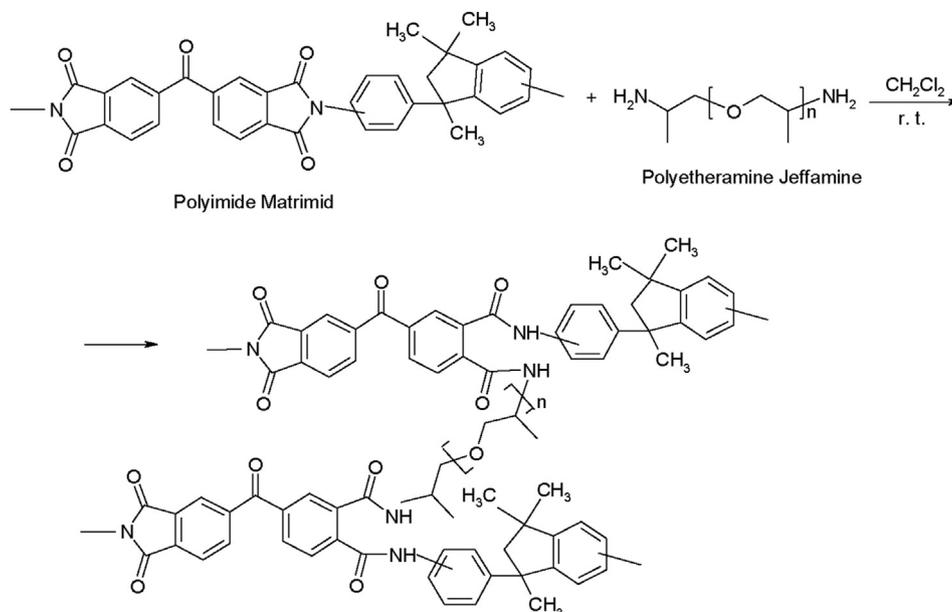
Thermal gravimetric analysis (TGA) was made using a Q-1500D thermal analyzer. About  $100\text{ mg}$  of each sample was heated from  $30\text{ }^\circ\text{C}$  to  $700\text{ }^\circ\text{C}$  with the heating rate of  $10\text{ }^\circ\text{C/min}$  in air.

The ionic conductivity of ionic liquid and PI/BAIM-TFSI composite membranes was measured with the help of impedance spectrometer Solartron SI 1260 in temperature range from  $25\text{ }^\circ\text{C}$  to  $160\text{ }^\circ\text{C}$ .

### 3. Results and discussion

#### 3.1. Infrared characterization of PI/BAIM-TFSI composite membranes

FTIR is a widely and reliable technique used to characterize very complex mixtures and specific interactions in polymer blend systems by looking into wavenumbers, shape, and intensity of specific



**Scheme 2.** Cross-linking of polyimide Matrimid with polyetheramine Jeffamine.

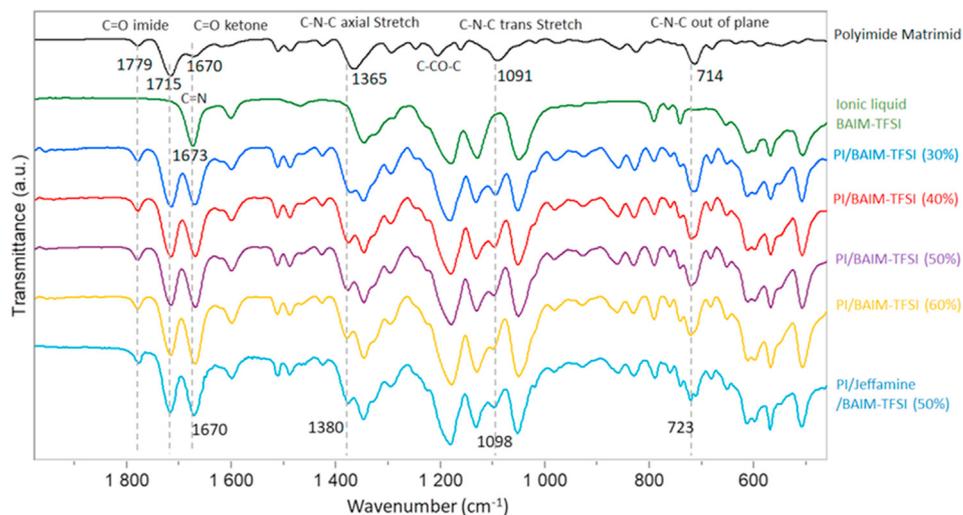


Fig. 1. IR spectra of polyimide Matrimid and its composites with BAIM-TFSI.

functional groups. FTIR-ATR spectra of Matrimid, BAIM-TFSI, and their composites are presented in Fig. 1.

The spectrum of pure Matrimid contains characteristic bands at  $1779\text{ cm}^{-1}$  and  $1715\text{ cm}^{-1}$  assigned to asymmetric and symmetric stretching modes of imide C=O groups, respectively, and a small intensity band at  $1670\text{ cm}^{-1}$  is attributed to the stretching vibrations of ketone C=O group [38–40]. The strong bands at  $1365\text{ cm}^{-1}$  and  $1091\text{ cm}^{-1}$  are commonly attributed to the C–N–C axial and *trans* stretching modes, respectively, and the band at  $714\text{ cm}^{-1}$ —to the out-of-plane bending vibration of the C–N–C group.

For the pure ionic liquid BAIM-TFSI, the main characteristic bands in the range of  $2700\text{--}4000\text{ cm}^{-1}$  are the N–H stretching mode at  $3366\text{ cm}^{-1}$ , the symmetric and asymmetric stretching vibrations of the methylene groups at  $2880\text{ cm}^{-1}$  and  $2940\text{ cm}^{-1}$ , and the asymmetric stretching vibrations of the methyl group at  $2966\text{ cm}^{-1}$ . In Fig. 1, the strong intensity bands are located at  $1673\text{ cm}^{-1}$  for the C=N stretching vibration mode, at  $1346\text{ cm}^{-1}$  and  $1129\text{ cm}^{-1}$  for the SO<sub>2</sub> antisymmetric and symmetric stretching modes and at  $1180\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  for CF<sub>3</sub> antisymmetric stretching and the C–C stretching modes, respectively [41].

For PI/BAIM-TFSI composite films, no significant change was observed either in peak position or intensity of the bands corresponding to vibrations of both ketone and imide C=O groups (Fig. 1). This may indicate the absence of hydrogen bonding between N–H groups of BAIM-TFSI and C=O groups of Matrimid. This result is likely owing to the self-association of PI macromolecules because of the formation of charge-transfer complex between carbonyl groups and imide nitrogen [42] (Scheme 2). On the other hand, specific interactions between aromatic rings with their  $\pi$  electronic sextet lead to parallel and planar orientation of individual chains to each other. The increased inter-chain attractive forces can thus induce a better packing of the polymer chains, leading to an increase in the rigidity of the composite and, therefore, in the glass transition temperature.

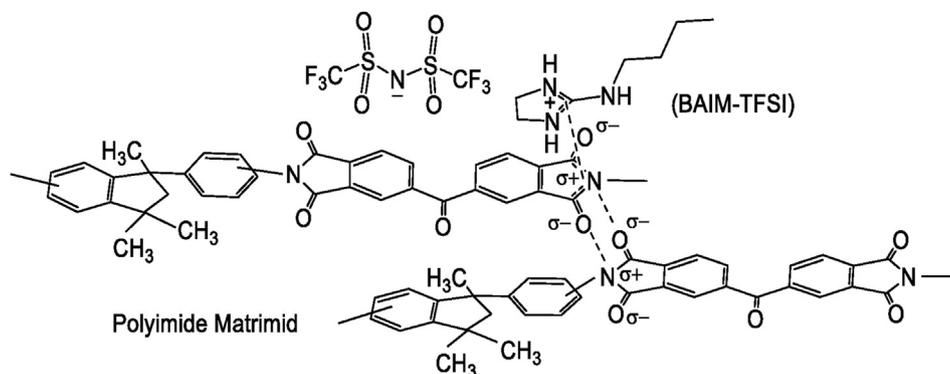
With the introduction of BAIM-TFSI, the IR spectra of composite films revealed that the C–N–C vibrational modes of imide cycle were shifted to higher wavenumber: from  $1365$  to  $1380\text{ cm}^{-1}$ , from  $1091$  to  $1098\text{ cm}^{-1}$ , and from  $714$  to  $723\text{ cm}^{-1}$  (Fig. 1). In addition, a shift of the C=N vibrations of the pure ionic liquid was observed toward lower wavenumber. According to these results, it can be suggested that  $\pi$ - $\pi$  interaction between imidazolium cation and imide cycle of Matrimid occurs (Scheme 3). Such physicochemical

interactions can affect both the compatibility of BAIM-TFSI with polymer matrix and the self-association of PI macromolecules.

### 3.2. Mechanical and thermal analysis of PI/BAIM-TFSI composites

The results of tensile testing of PI-based composite films containing different amount of ionic liquid are summarized in Table 1. The obtained results clearly indicate that PI/BAIM-TFSI composites have mechanical properties similar to the neat polymer and this for ionic liquid content up to 50 wt%. The low values of elongation at break for all composites confirm the high material rigidity. For PI/BAIM-TFSI (60%) films, the drop of tensile strength by more than 50% was observed. It is also interesting to note that the introduction of 30% of ionic liquid leads to a significant improvement of the tensile strength of Matrimid. PI films cross-linked with 10 mol% of polyetheramine Jeffamine also showed significantly improved tensile strength compared with neat polymer (Table 1). However, cross-linked PI containing 50% of ionic liquid has similar mechanical properties as PI/BAIM-TFSI (50%). The prepared dense composite membranes have much better tensile strength (at least 50%–70% more) compared with PEMs based on sulfonated PI/PIL [24] or porous Matrimid/PIL [27].

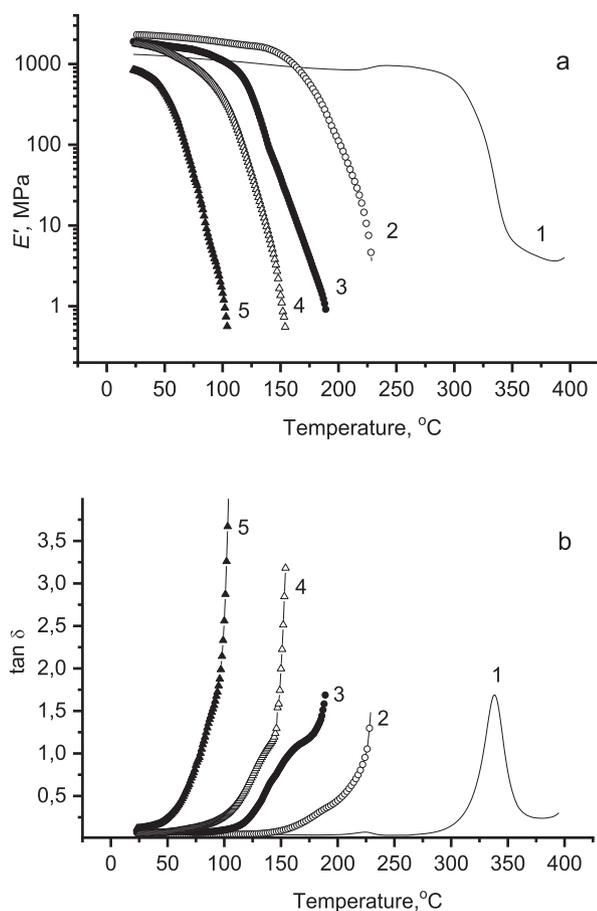
DMA study was further performed to assess the mechanical response of PI/BAIM-TFSI membranes to higher temperatures. PI Matrimid has high storage modulus  $E'$  ( $1320\text{--}630\text{ MPa}$ ; Fig. 2a, curve 1) and low values of  $\tan \delta$  (Fig. 2b, curve 1) in the temperature range  $20\text{--}300\text{ }^{\circ}\text{C}$ , indicating its excellent elastic properties for the use as polymer matrix for PEM. PI/BAIM-TFSI composite membranes with ionic liquid content up to 50% showed significantly increased  $E'$  values at room temperature, compared with neat polymer (Fig. 2a, curves 2–4, Table 2). Moreover, PI membrane containing 30% of BAIM-TFSI demonstrated improved elastic properties at elevated temperatures up to  $150\text{ }^{\circ}\text{C}$  (Fig. 2a, curves 1 and 2). At a higher ionic liquid content of 40% and 50%, this effect was also observed but in narrowed temperature range (Fig. 2a, curves 3 and 4). Probably, increased stiffness of PI/BAIM-TFSI composites is caused by the increasing of the packing density of PI macromolecules below glass transition temperature because of their physicochemical interaction with 2-butylaminoimidazolium cation of ionic liquid (Scheme 2). However, the increase of BAIM-TFSI content in PI films leads to noticeable reduction of temperature at which drop in storage modulus begins (Fig. 2a, curves 2–5). This is also



**Scheme 3.** Possible physicochemical interactions between PI and protic ionic liquid.

**Table 1**  
Mechanical properties of PI/BAIM-TFSI composite films.

Sample	Tensile strength, MPa	Elongation at break, %
PI	37.0 ± 1.0	7.2 ± 0.5
PI/BAIM-TFSI (30%)	72.5 ± 1.5	8.4 ± 1.5
PI/BAIM-TFSI (40%)	36.5 ± 1.0	8.0 ± 0.5
PI/BAIM-TFSI (50%)	32.6 ± 2.0	12.0 ± 2.5
PI/BAIM-TFSI (60%)	16.0 ± 2.0	12.5 ± 1.5
PI/Jeffamine (10% mol)	69.2 ± 2.0	9.3 ± 2.5
PI/Jeffamine/BAIM-TFSI (50%)	35.0 ± 1.0	7.5 ± 2.5
PI/Jeffamine/BAIM-TFSI (60%)	25.0 ± 2.0	8.0 ± 1.5



**Fig. 2.** DMA curves of  $E'$  (a) and  $\tan \delta$  (b): 1, polyimide Matrimid; 2, PI/BAIM-TFSI (30%); 3, PI/BAIM-TFSI (40%); 4, PI/BAIM-TFSI (50%); 5, PI/BAIM-TFSI (60%).

accompanied by a sharp increase in  $\tan \delta$  value (Fig. 2b, curves 2–5). These effects indicate a plasticizing effect of the ionic liquid on PI. Although significant reduction of storage modulus was observed for PI/BAIM-TFSI (40%) membrane above 120 °C (Fig. 2a, curve 3), this membrane still has  $E'$  value comparable to those reported for commercial Nafion membranes [43–45]. Further increase of ionic liquid content leads to a narrowing of the temperature range of acceptable mechanical properties to 120 °C with 50% content BAIM-TFSI and to 70 °C with 60% BAIM-TFSI (Fig. 2a, curves 4 and 5, Table 2).

The glass transition temperature ( $T_g$ ) of neat Matrimid determined by the position of the maximum of the loss factor  $\tan \delta$  (Fig. 2b, curve 1) was found to be 335 °C, indicating a high stiffness of polymer macromolecules. However, PI/BAIM-TFSI composites do not demonstrate distinct relaxation maximum on the temperature dependence of  $\tan \delta$  (Fig. 2b, curves 2–5). Such a result can be explained by high plasticization effect of ionic liquid. Indeed, viscous flow in the material can develop so quickly that the glass transition does not have time to be fixed. Thus, the temperature at which  $\tan \delta$  begins to rise can be defined as glass transition onset ( $T_{onset}$ ).

Previous studies of polymer electrolyte membranes based on sulfonated PIs and PILs have shown that the ionic liquid content of at least 50%–60% is required to reach sufficient level of ionic conductivity at elevated temperatures [24,26,28]. Therefore, we have tried to improve elastic properties of PI/BAIM-TFSI membranes with the same ionic liquid content by using partially cross-linked PI as polymer matrix. As one can see from Fig. 3a (curve 1) and Table 2, cross-linking of PI with 10 mol% of polyetheramine Jeffamine D-400 significantly improved its storage modulus both at room and elevated temperatures. This effect was not observed for lower content (5 mol%) of cross-linking agent (not shown). It should be noted that the glass transition temperature of PI/Jeffamine is 30 °C lower compared with neat PI (Table 2). The opening of imide cycles in PI macromolecules after their partial cross-linking with flexible chains of Jeffamine can lead to an increase of the free volume in the polymer matrix (Scheme 2). Therefore, the mobility of molecular chains increases, resulting in a reduction of  $T_g$ . At the same time, the presence of intermolecular cross-linking increases the resistance of material to deformation.

Similar to PI/BAIM-TFSI composites, there is no distinct relaxation maximum on  $\tan \delta = f(T)$  dependences for PI/Jeffamine/BAIM-TFSI films (Fig. 3b, curves 2, 3).  $T_{onset}$  value was also found to be significantly reduced with increasing ionic liquid content, indicating a strong plasticizing effect of BAIM-TFSI (Fig. 3, Table 2). However, in contrast to PI/BAIM-TFSI (50%) composite, PI/Jeffamine/BAIM-TFSI (50%) membrane showed reasonable  $E'$  value of 300 MPa at 130 °C (Table 2), which is comparable with those reported for commercial proton-

**Table 2**  
Viscoelastic characteristics of PI/BAIM-TFSI membranes.

Sample	$T_g$ , °C	$T_{onset}$ , °C	$E'_{T=25}$ °C, MPa	$E'_{T=120}$ °C, MPa	$E'_{T=130}$ °C, MPa	$E'_{T=140}$ °C, MPa
PI	335	300	1320	1050	1015	980
PI/BAIM-TFSI (30%)	–	165	2304	1710	1652	1535
PI/BAIM-TFSI (40%)	–	120	1885	596	268	92
PI/BAIM-TFSI (50%)	–	88	1780	75	25	7.5
PI/BAIM-TFSI (60%)	–	50	828	–	–	–
PI/Jeffamine (10 mol%)	305	265	2087	1621	1573	1528
PI/Jeffamine/BAIM-TFSI (50%)	–	130	1633	450	300	156
PI/Jeffamine/BAIM-TFSI (60%)	–	65	1327	8.7	–	–

conducting membranes such as Nafion [43,45] or phosphoric acid impregnated PBI [46]. Further increase of ionic liquid content in cross-linked PI-based composite led to soft material with unsatisfactory elastic behavior (Fig. 3a, curve 3, Table 2). Thus, we limited maximum ionic liquid content to 50 wt% for studying the conductivity of PI/BAIM-TFSI membranes.

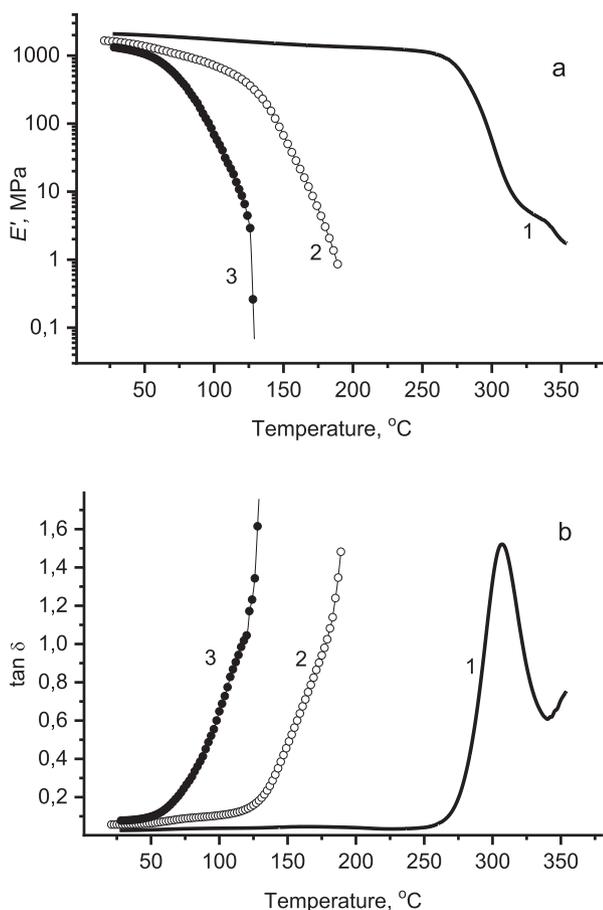
According to TGA data, BAIM-TFSI ionic liquid has the thermal degradation point (i.e., 5% weight loss) of 350 °C, with maximum rate at 456 °C (Fig. 4, curve 1, Table 3) that indicates sufficient thermal stability for high-temperature fuel cell applications. PI Matrimid has outstanding thermal properties being stable to at least 455 °C with maximum degradation rate at 595 °C (Fig. 4, curve 2). PI/BAIM-TFSI composites also showed high thermal stability (Fig. 4, curves 3–6) with thermal degradation points in the

temperature range 377 °C–397 °C, which were noticeably higher compared with pure PIL (Table 3).

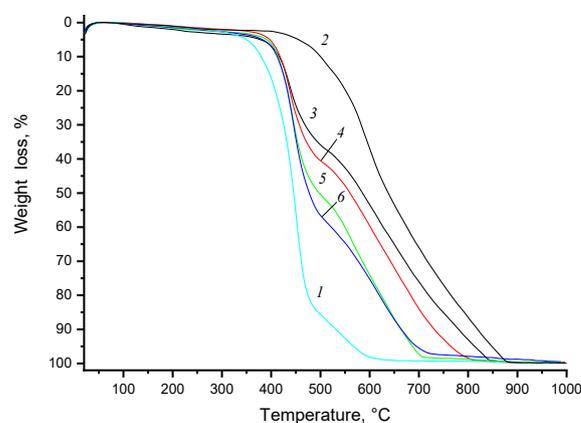
PI cross-linked with polyetheramine Jeffamine began to decompose at 318 °C, thus showing significantly reduced thermal stability than neat polymer (Fig. 5a). However, composite membranes based on cross-linked PI and BAIM-TFSI were found to have similar thermal properties as PI/BAIM-TFSI membranes (Fig. 5b, Table 3).

### 3.3. Ionic conductivity of PI/BAIM-TFSI composite membranes

The ionic conductivity of pure ionic liquid and PI/BAIM-TFSI composite membranes was measured in the temperature range of 25–160 °C (Fig. 6). The conductivity of BAIM-TFSI was found to be  $5 \times 10^{-3}$  S/cm at room temperature. This value increased by one order of magnitude below 100 °C (Table 4), reaching the value similar to that of other hydrophobic PILs with TFSI anion [16]. All studied PI/BAIM-TFSI membranes showed poor ionic conductivity at room temperature—from  $3.1 \times 10^{-9}$  S/cm to  $3.1 \times 10^{-6}$  S/cm. This is probably caused by low free volume of the system, which creates barriers for efficient proton transfer. At elevated temperatures, the conductivity of composite films significantly increased by three to five orders of magnitude, depending on ionic liquid content (Fig. 6, curves 2–4, Table 4). This may be explained by enhanced free ionic mobility of BAIM-TFSI in the membrane matrix [16,19]. Moreover, segmental motion of PI macromolecules because of plasticization effect of ionic liquid at temperatures above 100 °C (Table 2) may also promote the formation of well-developed ionic channels. Accordingly, the minimal level of ionic conductivity ( $10^{-3}$  S/cm) required for PEM was reached for PI/BAIM-TFSI (40%) membrane at 145 °C and for PI/BAIM-TFSI (50%) membrane at



**Fig. 3.** DMA curves of  $E'$  (a) and  $\tan \delta$  (b): 1, PI/Jeffamine (10 mol%); 2, PI/Jeffamine/BAIM-TFSI (50%); 3, PI/Jeffamine/BAIM-TFSI (60%).



**Fig. 4.** TGA curves of BAIM-TFSI (1), PI (2), and PI/BAIM-TFSI with different ionic liquid content: 30% (3), 40% (4), 50% (5), and 60% (6).

**Table 3**  
TGA data for BAIM-TFSI and its composites with polyimide Matrimid.

Sample	T <sub>Δm=5%</sub> , °C	T <sub>Δm=10%</sub> , °C	T <sub>Δm=20%</sub> , °C	T <sub>Δm=50%</sub> , °C
BAIM-TFSI	350	380	408	445
PI	455	500	551	638
PI/BAIM-TFSI (30%)	377	416	440	585
PI/BAIM-TFSI (40%)	397	418	438	560
PI/BAIM-TFSI (50%)	391	414	433	497
PI/BAIM-TFSI (60%)	382	412	433	477
PI/Jeffamine (10 mol%)	318	426	523	641
PI/Jeffamine/BAIM-TFSI (50%)	370	417	441	525
PI/Jeffamine/BAIM-TFSI (60%)	379	409	429	478

120 °C (Fig. 6, curves 3 and 4, Table 4). The composite membrane based on cross-linked PI and BAIM-TFSI (50%) showed noticeably higher conductivity than PI/BAIM-TFSI (50%). Thus, the conductivity reached the level of 10<sup>-3</sup> S/cm at 60 °C and increased by one order of magnitude at 120 °C (Fig. 6, curve 5, Table 4). It is reasonable to assume that PI matrix, cross-linked with bulk and flexible Jeffamine molecules, has higher free volume compared with the linear PI matrix, thus promoting the formation of proton transfer channels.

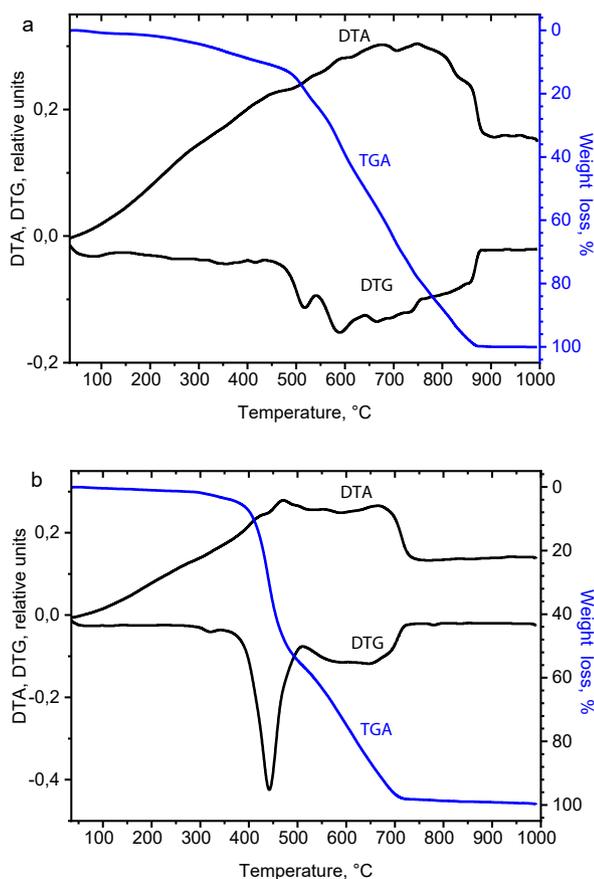
As previously described, two types of charge transport mechanism in PILs exist: vehicle (molecular diffusion) and Grotthuss-type (proton migration in the hydrogen-bonded networks). Imidazolium cation of BAIM-TFSI contains three exchangeable protons, which may ensure efficient proton hopping conduction mechanism. The last one involves thermal activation and follows Arrhenius law as a function of temperature:

$$\ln \sigma = -E_a/RT + \ln \sigma_0$$

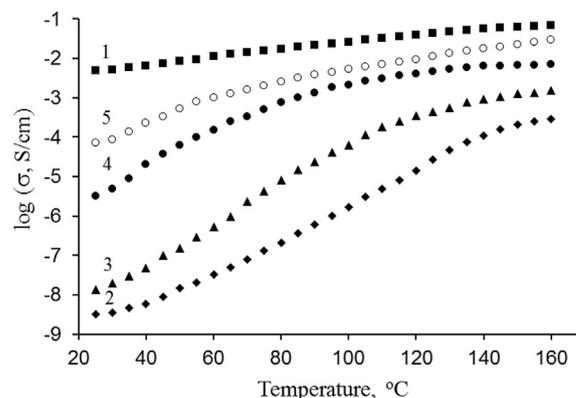
where  $\sigma_0$  is the maximum conductivity at infinite temperature (S/cm),  $E_a$  is the activation energy (kJ/mol), which indicates the energy needed for an ion to jump to a free hole, R is the universal gas constant (8.314 J/(mol·K)), and T is the absolute temperature (K).

Thus, the activation energy for conductivity characterizes the difficulty level of ions migration under the electric field. In the Arrhenius diagram (Fig. 7), temperature dependence of ionic conductivity ( $\ln \sigma$  vs 1000/T) is linear in the temperature range 60 °C–130 °C for both pure BAIM-TFSI and PI/BAIM-TFSI membranes. The activation energy  $E_a$  calculated from the slope value (Fig. 7, line 1) is 22 kJ/mol for pure ionic liquid. This value is higher compared with other reported guanidinium-based PILs—1-butylguanidinium tetrafluoroborate ( $E_a = 17$  kJ/mol) [35] and guanidinium nonaflate ( $E_a = 19$  kJ/mol) [47]. This indicates less mobility in proton transfer of the bulk 1-butylaminoimidazolium cation with lower content of exchangeable protons, compared with guanidinium-based ionic liquids.

The Arrhenius plots for PI/BAIM-TFSI membranes reveal steeper slopes compared with the ionic liquid (Fig. 7, lines 2–5), which indicates significantly higher activation energy for ionic conductivity. Thus, calculated  $E_a$  values were found to be 113, 80, and 57 kJ/mol for PI/BAIM-TFSI composites containing 30%, 40%, and 50% of ionic liquid, respectively. The Grotthuss-type mechanism of proton conduction is known to involve activation energies below 0.4 eV (<38.5 kJ/mol), whereas the transport of larger ionic species (vehicle mechanism) requires higher energy ( $E_a > 0.4$  eV) [48]. Thus, the obtained data clearly indicate that the proton transport in PI/BAIM-TFSI membranes is realized mainly by vehicle mechanism. The content of 50% of ionic liquid



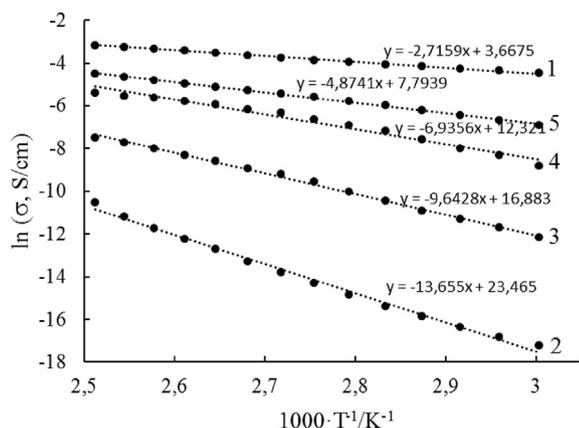
**Fig. 5.** TGA curves of polyimide Matrimid cross-linked with polyetheramine Jeffamine (a) and PI/Jeffamine/BAIM-TFSI (50%) composite (b).



**Fig. 6.** Ionic conductivity (at frequency of 1 kHz) as a function of temperature (heating process) for BAIM-TFSI (1), PI/BAIM-TFSI composite membranes containing 30% BAIM-TFSI (2), 40% BAIM-TFSI (3), 50% BAIM-TFSI (4), and PI/Jeffamine/BAIM-TFSI (50%) (5) membranes.

**Table 4**  
Ionic conductivity of protic ionic liquid and PI/BAIM-TFSI composite membranes as a function of temperature.

Sample	$\sigma$ , S/cm			
	25 °C	120 °C	130 °C	140 °C
BAIM-TFSI	$5.0 \times 10^{-3}$	$4.0 \times 10^{-2}$	$4.6 \times 10^{-2}$	$5.6 \times 10^{-2}$
PI/BAIM-TFSI (30 wt%)	$3.1 \times 10^{-9}$	$1.6 \times 10^{-5}$	$5.0 \times 10^{-5}$	$1.1 \times 10^{-4}$
PI/BAIM-TFSI (40 wt%)	$1.6 \times 10^{-8}$	$3.5 \times 10^{-4}$	$5.0 \times 10^{-4}$	$8.0 \times 10^{-4}$
PI/BAIM-TFSI (50 wt%)	$3.1 \times 10^{-6}$	$4.0 \times 10^{-3}$	$5.3 \times 10^{-3}$	$6.3 \times 10^{-3}$
PI/Jeffamine/BAIM-TFSI (50%)	$2.7 \times 10^{-5}$	$7.9 \times 10^{-3}$	$1.1 \times 10^{-2}$	$1.6 \times 10^{-2}$



**Fig. 7.** Arrhenius plots of ionic conductivity for BAIM-TFSI (1), PI/BAIM-TFSI membrane containing 30% BAIM-TFSI (2), 40% BAIM-TFSI (3), 50% BAIM-TFSI (4), and PI/Jeffamine/BAIM-TFSI (50%) membrane (5).

in dielectric PI matrix is probably insufficient to realize the hopping mechanism of proton transport, which was found to dominate in commercial PBI and Nafion membranes impregnated with commonly used PILs TEA-TF or [dema][TfO] [49,50]. It can be explained by the fact that both PBI or Nafion polymer matrix and PIL participate in the proton transport, whereas in PI/BAIM-TFSI membranes, the polymer matrix does not contain proton-conducting sites. However, PI/Jeffamine/BAIM-TFSI (50%) membrane was found to have an  $E_a$  value of 40 kJ/mol, significantly lower than the value found for the PI/BAIM-TFSI (50%) composite (Fig. 7, lines 4, 5). In this system, the Grotthuss-type mechanism of proton conduction may be expected to occur. Similar calculated values of activation energy of ionic conductivity (~40 kJ/mol) have been reported for PBI/[dema][TfO] [49] and SPI/2-undecylimidazole [8] composites in which proton transfer is known to be realized mainly by hopping mechanism. It is interesting to note that the ionic conductivity of PI/Jeffamine/BAIM-TFSI (50%) membrane above 120 °C (Fig. 6, curve 5, Table 4) is similar to those for composite membranes based on SPIs containing 50% of PIL [24,26]. This indicates the possibility of manufacturing proton-conducting membranes based on PILs without the use of an expensive stage of their sulfonation.

#### 4. Conclusions

New hydrophobic protic ionic liquid comprising cyclic guanidinium cation, BAIM-TFSI, has been synthesized. The ionic liquid combines both high thermal stability (to at least 350 °C) and ionic conductivity ( $5.6 \times 10^{-2}$  S/cm at 140 °C). It has excellent compatibility with commercial PI Matrimid, allowing the preparation of composite films containing from 30 to 60 wt% of BAIM-TFSI by casting from methylene chloride solutions. TGA results indicate

good thermal stability of PI/BAIM-TFSI composites having thermal degradation points in the range of 377 °C–397 °C. According to the results of mechanical testing, the addition of BAIM-TFSI up to 50% in PI films does not cause a noticeable deterioration of tensile strength of the polymer. Moreover, DMA analysis revealed significantly improved viscoelastic properties of PI/BAIM-TFSI membranes at room temperature compared with Matrimid. At lowest ionic liquid content of 30%, the tensile strength and storage modulus  $E'$  of the composite were found to increase by 94% and 74%, respectively. This is probably caused by denser packing of PI macromolecules as a result of their physicochemical interactions with BAIM-TFSI. However, significant reduction of  $E'$  value for PI/BAIM-TFSI films was observed above 100 °C because of plasticization effect of the ionic liquid on polymer matrix. The results of electrochemical impedance study of PI/BAIM-TFSI membranes have shown that the minimal level of ionic conductivity ( $10^{-3}$  S/cm) required for PEM can be reached for PI/BAIM-TFSI (40%) at 145 °C or for PI/BAIM-TFSI (50%) at 120 °C.

To improve elastic properties of composite membrane, PI was cross-linked with polyetheramine Jeffamine D-400 (10 mol%) in methylene chloride solution at room temperature. This approach allowed to prepare PI/Jeffamine/BAIM-TFSI (50%) membrane having  $E'$  value of 300 MPa at 130 °C, in contrast to PI/BAIM-TFSI (50%) composite, which has storage modulus of 25 MPa. The ionic conductivity of composite membrane reached the level of  $10^{-2}$  S/cm at 130 °C that makes it potentially available for the use in medium-temperature fuel cells operating in water-free conditions. The activation energy  $E_a$  values calculated from the Arrhenius plot for pure ionic liquid BAIM-TFSI as well as for PI/Jeffamine/BAIM-TFSI (50%) membrane were found to be 22 kJ/mol and 40 kJ/mol, respectively. On the basis of these data, one can conclude that the proton transport in both ionic liquid and PI-based composite membrane is dominated by Grotthuss-type (hopping) mechanism. It is also important to note that PI/Jeffamine/BAIM-TFSI membrane showed similar ionic conductivity at elevated temperatures as previously reported PEMs based on sulfonated aromatic PILs and PILs. This approach, based on simple and inexpensive preparation methods, opens up really promising perspectives to develop proton-conducting membranes for fuel cell applications based on commercial PI Matrimid. Additional research is nevertheless underway to improve room temperature conductivity of the elaborated membranes, which is insufficient for normal operation of fuel cells below 100 °C.

#### Authors' contributions

S.R. synthesized ionic liquid and cross-linked polyimide and wrote the article. J.-F.B. performed infrared analysis and wrote the article. S.M. performed electrophysical investigations. O.T. prepared composite membranes. N.B. performed dynamic mechanical analysis. Tetiana T.C. performed thermal investigations. M.F. analyzed the data. K.F. conceived and designed the experiments and analyzed the data

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtchem.2021.100453>.

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