Journal of Membrane Science 549 (2018) 267–274

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Effect of polymer molecular weight on the physical properties and CO_2/N_2 separation of pyrrolidinium-based poly(ionic liquid) membranes

Liliana C. Tomé[a,b,*], Diogo C. Guerreiro[a], Raquel M. Teodoro[a], Vítor D. Alves[c], Isabel M. Marrucho[a,b,*]

[a] Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal
[b] Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Avenida Rovisco Pais, 1049-001 Lisboa, Portugal
[c] LEAF – Linking Landscape, Environment, Agriculture and Food, Instituto Superior de Agronomia, Universidade de Lisboa, Tapada da Ajuda, 1349-017 Lisboa, Portugal

ARTICLE INFO

Keywords:
PIL–IL composites
Polymer molecular weight
Membrane forming ability
Thermal analysis
Mechanical properties
Gas permeation

ABSTRACT

Aiming at investigating the effect of the polymer molecular weight (M_w) on the physical and gas permeation properties of poly(ionic liquid)-ionic liquid (PIL–IL) composites, this work focuses on membranes based on variable M_w pyrrolidinium-PILs having $[C(CN)_3]^-$ as counter-anion and different amounts (20, 40 and 60 wt%) of free $[C_2mim][C(CN)_3]$ IL. Although all the prepared composite materials have high thermal stability (T_{onset} > 556 K) for post-combustion CO_2 separation, the evaluation of the film forming ability shows that it is not possible to obtain free standing PIL–IL membranes using the Low M_w PIL (average < 100 kDa). The formed Medium M_w (average 200 – 350 kDa) and High M_w (average 400 – 500 kDa) PIL–IL membranes present similar mechanical properties in terms of Young´s modulus, tensile strength and elongation at break. The gas permeabilities and diffusivities are dependent on the M_w of the PIL used. The Medium M_w PIL–IL membranes display higher CO_2 permeabilities (14.6 – 542 Barrer) than those (8.0–439 Barrer) observed for High M_w PIL–IL composites. Despite the M_w of the PIL used, the incorporation of high free IL contents increases both CO_2 permeability and CO_2/N_2 permselectivity. Consequently, the finest CO_2/N_2 separation performances, overcoming the 2008 upper bound in the Robeson plot, were obtained for the High and Medium M_w PIL–60 IL composites, respectively, with CO_2 permeabilities of 439 and 542 Barrer and CO_2/N_2 permselectivities of 64.4 and 54.0.

1. Introduction

Among the broad range of diverse membrane materials investigated for gas separation over the past few years [1–3], polymeric ionic liquids or poly(ionic liquid)s (PILs), a subclass of polyelectrolytes that combine the chemical tunability of ionic liquids (ILs) with the common features of polymers [4], have emerged as new versatile task-specific materials for the development of high performance CO_2 separation membranes [5–7]. The potential of these functional ionic polymers has been exploited using different membrane arrangements, such as neat PIL membranes [8–11], PIL–IL composite membranes [12–14], PIL copolymer membranes [15–17], and PIL–IL–inorganic particle mixed matrix membranes [18–20].

The development of PIL–IL composite membranes, which combine the best properties of both ILs and PILs, allowed membranes with high CO_2 permeability and CO_2/N_2 permselectivity, as well as good mechanical properties. The proof-of concept was published by Bara et al. [21], who prepared PIL–IL composite membranes by polymerization of an IL monomer in the presence of 20 wt% of free (non-polymerizable) IL. The improved CO_2 separation performances obtained in the presence of free IL [22,23] inspired other researchers to pursue this strategy. The majority of the PIL–IL composite membranes studied so far were prepared using PILs composed of imidazolium cation moieties in their polymeric backbone and fluorinated or cyano-functionalized as counter-anions [24–27].

Later on, and in order to understand the influence of the PIL polycation, our group investigated the gas permeation properties of PIL–IL membrane materials based on PILs having different cation functionalities, such as imidazolium, pyridinium, pyrrolidinium, ammonium and cholinium [28]. The results showed that depending on the chemical structure of the polycationic PIL, the polymer chains interact and pack differently, thus affecting the gas transport. Nevertheless, polycation variations alone cannot promote the CO_2 permeability improvements needed for PIL–IL membranes to be considered competitive [28]. In light of this fact, and also considering that pyrrolidinium-based PILs can be prepared by anion metathesis reactions from a commercially

* Corresponding authors at: Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Av. da República, 2780-157 Oeiras, Portugal.
E-mail addresses: liliana.tome@itqb.unl.pt (L.C. Tomé), isabel.marrucho@tecnico.ulisboa.pt (I.M. Marrucho).

https://doi.org/10.1016/j.memsci.2017.12.019
Received 20 October 2017; Received in revised form 30 November 2017; Accepted 9 December 2017
Available online 10 December 2017
0376-7388/ © 2017 Elsevier B.V. All rights reserved.

available polyelectrolyte [29], which is a very simple procedure when compared to those used for the aforementioned polycationic PILs, the pyrrolidinium polycation was selected to continue our studies. PIL–IL composite membranes comprising pyrrolidinium polymer matrices with different counter-anions, namely $[NTf_2]^-$ [30], $[N(CN)_2]^-$, $[C(CN)_3]^-$ and $[B(CN)_4]^-$ [31], or counter-anions mixtures [32], were prepared by solvent casting and their gas permeation properties evaluated. In general, the obtained results not only demonstrated that the CO_2 permeability and permselectivity properties of PIL–IL membranes can be tuned by increasing the IL content [30] or using PIL random copolymers with different counter-anion mixtures [32], but also highlighted for the first time a PIL–IL composite membrane (based on $[C(CN)_3]^-$) overcoming the Robeson 2008 upper bound for CO_2/N_2 separation [31].

Despite the fairly intense amount of literature on the preparation, evaluation and comparison of CO_2/N_2 separation performance through PIL–IL membranes containing structurally different ILs and PILs, it is also important to consider other properties when selecting a membrane material for gas separation applications. In particular, for PIL–IL composite membranes, material properties such as processability, thermal and mechanical stability can be affected by PIL specific features, such as, for instance, the polymer molecular weight that, to the best of our knowledge, has not yet been addressed.

Therefore, the aim of this work is to evaluate the effect of the PIL molecular weight (M_w) on the membrane forming ability, thermal and mechanical stability, as well as on the CO_2 permeability and permselectivity properties of PIL–IL composite membranes. For this purpose, pyrrolidinium-based PILs having $[C(CN)_3]^-$ as counter-anion and different M_w (Fig. 1), namely High M_w (average 400 – 500 kDa), Medium M_w (average 200 – 350 kDa) and Low M_w (average < 100 kDa), were first synthesized by straightforward anion exchange reactions from the corresponding commercially available polyelectrolyte precursors in the chloride form. Afterward, PIL–IL composite membranes containing different amounts (20, 40 and 60 wt%) of free $[C_2mim][C(CN)_3]$ IL were prepared and characterized. The choice of $[C(CN)_3]^-$ as both the PIL counter-anion and IL anion was dictated by its great CO_2 permeability and permselectivity [31,33], so that high performance PIL–IL composite membranes for CO_2/N_2 separation could be obtained.

2. Experimental section

2.1. Materials

Acetonitrile (99.8%) and poly(diallyldimethylammonium) chloride solutions with different molecular weights (M_w), particularly High M_w (average 400 – 500 kDa, 20 wt% in water), Medium M_w (average 200 – 350 kDa, 20 wt% in water) and Low M_w (average < 100 kDa, 35 wt% in water), were purchased from Sigma-Aldrich and used as received. IoLiTec GMbH supplied both the sodium tricyanomethanide ($NaC(CN)_3$) (98 wt% pure) and the 1-ethyl-3-methylimidazolium tricyanomethanide ($[C_2mim][C(CN)_3]$) (> 98 wt% pure), which were dried under vacuum (1 Pa) at moderate temperature (~ 318 K) for at least 2 days prior to use. The water used was double distilled. The carbon dioxide (CO_2) and nitrogen (N_2) were provided by Air Liquide and were of at least 99.99% purity.

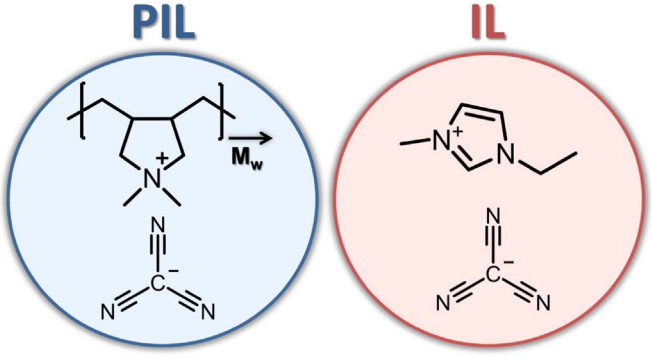

Fig. 1. Chemical structures of the variable molecular weight poly(ionic liquid)s (PILs) and the ionic liquid (IL) used to prepare the composite membranes.

2.2. Synthesis of PILs

Poly(ionic liquid)s (PILs), with pyrrolidinium pendant units, $[C(CN)_3]^-$ as counter-anion, and different M_w (Fig. 1), were synthesized by anion metathesis reactions from the commercially available poly (diallyldimethylammonium) chloride precursors, following a procedure described elsewhere [31]. The resulting white solid PILs, namely the poly($[Pyr_{11}][C(CN)_3]$) with Low M_w, Medium M_w and High M_w, respectively, were washed with water, filtered and dried in a vacuum oven at 318 K (yields > 85%).

2.3. Preparation of PIL–IL membranes

Composite membranes (Fig. 2) based on the variable molecular weight PILs and different amounts of the free IL $[C_2mim][C(CN)_3]$ were prepared by solvent casting. First, 6 (w/v)% solutions of each PIL in acetonitrile were prepared. Afterwards, the $[C_2mim][C(CN)_3]$ was added in order to obtain solutions with 20, 40 and 60 wt% of free IL to the PIL matrix. The solutions were magnetically stirred, until complete dissolution of both components, before being poured into Petri dishes and left for slow acetonitrile evaporation at 313 K for 2 days. The formed composite materials were then peeled out of the Petri dishes and dried in a ventilated oven at 333 K until constant weight was attained. The composition description of the prepared PIL–IL composites is presented in Table 1. The membrane thicknesses (120 – 230 μm) were measured using a digital micrometer (Mitutoyo, model MDE-25PJ, Japan).

2.4. Thermal analysis

Thermogravimetric analyses (TGA) of the neat PILs and their PIL–IL composites were performed on a TGA Q50 analyzer from TA instrument, under nitrogen atmosphere. The samples were heated at a constant rate of 10 K min^{-1}, from room temperature to 1073 K. The Universal Analysis software (version 4.4 A) was used to determine the onset (T_{onset}) and decomposition (T_{dec}) temperatures, as the temperatures at which the baseline slope changes during the heating, and at which 50% of weight loss was observed, respectively.

2.5. Mechanical analysis

Tensile assays were performed on a TA-XT plus texture analyzer (Stable Micro Systems, Surrey, England) at ambient conditions. The membrane test specimens (20 × 70 mm) were fixed with tensile grips A/TG and stretched at a deformation rate of 1 mm s^{-1} in tension mode. At least ten specimens were analyzed for each PIL–IL membrane sample. Tensile strength at break (stress, MPa) was determined as the ratio of the maximum force to the membrane initial cross-sectional area, while elongation at break (strain, %) was calculated as the ratio of the extension of the specimen upon rupture by its initial gauge length. The Young's modulus (elastic modulus, MPa) was obtained from the slope of the initial linear region in the stress-strain curve.

2.6. Gas permeation measurements

Single gas CO_2 and N_2 permeation measurements were performed using a time-lag apparatus, which is fully described elsewhere [30]. Initially, the membranes were evacuated inside the permeation cell for 12 h using an Edwards RV3 vacuum pump. Afterwards, the gas permeation measurements were conducted at 293 K with a trans-

Download English Version:

https://daneshyari.com/en/article/7020206

Download Persian Version:

https://daneshyari.com/article/7020206

Daneshyari.com