

Poly(Vinylimidazole-co-butyl acrylate) Membranes for CO₂ separation

Ting Song^{a, b}, Jing Deng^c, Liyuan Deng^c, Xiangping Zhang^b, Suojiang Zhang^b, Peter Szabo^a and Anders E. Daugaard^{a*}

^a Danish Polymer Center, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, 2800 Kgs. Lyngby, Denmark

^b Beijing Key Laboratory of Ionic Liquids Clean Process, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, 100190, China

^c Department of Chemical Engineering, Norwegian University of Science and Technology, 7491, Trondheim, Norway

Correspondence: adt@kt.dtu.dk; Tel.: +45-4525-6815

Abstract

Room temperature ionic liquids (RTILs) are known to exhibit high CO₂ solubility, which makes them interesting candidates for separation and purification of mixed gas streams. Particularly, RTILs based on imidazoles have shown very promising results. However, such systems are inherently brittle, which makes them too fragile for use in freestanding membranes. Therefore, the copolymerization of N-vinylimidazole (VIm) and butyl acrylate (BuA) were investigated, showing reactivity ratios of $r_{\text{BuA}}=1.91-2.02$ and $r_{\text{VIm}}=0.094-0.10$. Copolymers could be quarternized and crosslinked into thin film membranes in a one-pot reaction employing a mixture of mono and difunctional alkyl halides. Particularly, poly(VIm-co-BuA) (24:76), was found sufficiently flexible, and were crosslinked with a mixture of 1:8, 1:2 and 1:0 of 1,6-dibromohexane and 1-bromobutane, respectively. The one-pot process allows incorporation of 16 wt% free RTIL (BMIM Tf₂N) in the 1:0 ratio membranes. All membranes were tested for CO₂ separation from N₂ and CH₄, resulting in a permeability of CO₂ of 54.38 Barrer. By varying the crosslinking degree, it was observed that CO₂ permeability increased with decreasing the degree of crosslinking. Finally, films prepared with free RTIL led to an improvement of the gas separation performance, with CO₂ permeability increased from 33.71 to 38.77 Barrer and CO₂/N₂ permselectivity increased from 20.81 to 27.82.

Keywords: N-vinylimidazole; Butyl acrylate; Poly(ionic liquid); Crosslinking free-standing membrane; Gas separation.

1. Introduction

Room temperature ionic liquids (RTILs), which contain large and unsymmetrical organic cations and organic or inorganic anions, are molten salts at temperatures below 100 °C.[1] RTILs are popular in many fields, such as for batteries, in extractions, as catalyst and for separation due to their excellent chemical, thermal, and electrochemical stability, nonflammability and negligible volatility.[2][3] Additionally, the high selection of possible counterions, being cationic or anionic as well as hydrophilic/hydrophobic, endow RTILs tunable properties to match different applications. However, industrial application of RTILs has been limited due to their high viscosity, price and liquid morphology.[4] Therefore, it is attractive to combine RTILs with membrane technology, which presents advantages of lower energy costs, reduced volatility and easy reuse, to overcome the disadvantages of RTILs.[5] RTILs, especially imidazole based RTILs, possess better solubility to CO₂ than other light gases, such as N₂ and CH₄. [6] Therefore, RTILs have been widely exploited to separate CO₂ from natural gas and flue gas over the past two decades. Initially, RTILs were used in supported ionic liquid membrane (SILM), where commercially available membranes have been filled with a range of RTILs, showing CO₂ separation performance with ideal CO₂ permeabilities of more than 1000 Barrers and CO₂/N₂ permselectivity of more than 20.[7] RTILs were immobilized in porous membranes with weak capillary forces, where loss of RTILs through leakage from the membrane support is significant.[8] This instability of SILMs under high pressure has limited their industrial application, even though SILMs have shown promising CO₂ separation performance.[9] In order to overcome the shortcomings of SILMs, Noble et al. [9][10] polymerized RTILs monomers with acrylic, styrenic or vinyl imidazole on nanoporous support membranes to form stable poly(RTIL) membranes for gas separation. Poly(RTIL) membranes possess mechanical stability and efficiently immobilize the RTILs in contrast to SILM, but exhibit much lower gas permeability and diffusivity. That is attributed to a lower fractional free volume of the dense poly(RTIL) compared to that of free RTILs.[4] According to previous investigations, combinations of

poly(RTIL) and RTILs in composite membranes improved CO₂ permeability by 400 % relative to neat poly(RTIL) membrane due to the introduction of free RTILs.[11] However, imidazole-based poly(RTIL) are generally too brittle to form free-standing membranes and need porous polymer membranes as support. We therefore in this study investigated the copolymerization of N-vinyl imidazole (VIm) and butyl acrylate, to facilitate preparation of soft copolymers that could act as precursors for poly(RTIL) membranes. By use of a simple one-pot quaternization and crosslinking reaction, these copolymers are used for preparation of soft, flexible, free-standing membranes, which were investigated for gas separation properties.

2. Experimental

2.1 Chemicals

Butyl acrylate, N-vinylimidazole, 2,2'-azobis(2-methylpropionitrile) (AIBN), dimethylformamide (DMF), 1, 6-dibromohexane and 1-bromobutane were purchased from Sigma-Aldrich. Ethanol was from VWR. The ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM] [Tf₂N]) was purchased from Iolitec Ionic Liquids Technologies company. Inhibitors were removed from the monomers by passing them through neutral alumina prior to use. All other chemicals were used as received.

CO₂, N₂, and CH₄ gases were purchased from AGA Co. Ltd with a purity grade of 99.999%.

2.2 General synthesis of polymers, exemplified by poly(vinylimidazole-co-butyl acrylate) (exemplified with poly(VIm-co-BuA) 48:52)

AIBN (0.087 g, 0.53 mmol) was dissolved in DMF (10 mL) and monomers, 1-vinylimidazole (1.9 g, 20.2 mmol) and butyl acrylate (2.6 g, 20.3 mmol), were added into the flask. The reaction mixture was bubbled with nitrogen for 20 min to remove all traces of oxygen. The polymerization mixture stirred under nitrogen using a magnetic stirrer for 10 h at 70 °C. During the polymerization the viscosity of the mixture gradually increased. The crude product was purified by precipitation into ether, it was redissolved in EtOH and precipitated into ether again. The product copolymer was then dried in *vacuo* until its mass became constant. Poly(vinylimidazole) (poly(VIm)) and poly(butyl acrylate) (poly(BuA)) and other copolymers were also synthesized using the general method (see supporting information for experimental and analytical data).

IR (cm⁻¹): 3111cm⁻¹ (C=C-H stretching), 3012-2844 cm⁻¹, 1451cm⁻¹ (-CH₂- symmetric and asymmetric stretching), 1727 cm⁻¹ and 1160 cm⁻¹ (stretching vibration C=O and C-O-C in acrylate group), 1494 cm⁻¹ (N=C-H stretching), 1267 cm⁻¹ and 1223cm⁻¹ (ring vibrations), 912 cm⁻¹ (C-H out of plane bending), 664 cm⁻¹ (ring torsion), 632 cm⁻¹ (C=C-H and N=C-H wagging);

¹H-NMR (δ_H, ppm, CDCl₃): 7.4-6.4 (m, 3H), 4.1-3.5 (m, 2H), 2.27-1.45(m, 6H), 1.46 (m, 2H), 1.26 (m, 2H), 0.87 (m, 3H).

2.3 General procedure for preparation of crosslinked poly(VIm-co-BuA) membranes (exemplified with the 20% crosslinked membrane).

Poly(VIm-co-BuA) (24:76, 1.5 g, 3.0 mmol functional group) was dissolved in ethanol (12 mL) by stirring overnight. Then 1,6-dibromohexane (0.09 g, 0.37 mmol) and 1-bromobutane (0.42 g, 3.01 mmol) (The details for the other compositions are showed in the supporting information) were introduced into the copolymer solution to prepare membranes with different crosslinking degree, and the mixture was stirred for additionally 1 h. The solution was degassed by ultrasonication for 10 min and casted in a Teflon petri dish. The casting solution was allowed to evaporate at ambient conditions in a fume hood. To remove entrapped residues of solvent, the casted membrane was dried *in vacuo* at 65 °C for 6 h. Procedures for all membranes can be seen in the supporting information.

2.4 Characterization methods

¹H Nuclear magnetic resonance (NMR) spectra of the as prepared poly(VIm-co-BuA) were carried out on a Bruker Avance 300 MHz spectrometer using deuterated dimethylsulfoxide or chloroform as solvents. Fourier transform infrared (FT-IR) was performed with a Niclet is50 ATR spectrometer with a diamond crystal from Thermo Scientific in the range of 4000-400 cm⁻¹. Gel permeation chromatography (GPC) was carried out on Viscotek 200 instrument with PLgel mixed-D columns and refractive index detector. The measurement took place with THF (1 ml/min) as mobile phase at room temperature. Thermo gravimetric analysis (TGA) was performed in a nitrogen atmosphere on a Discovery TGA from TA Instruments Differential scanning calorimetry (DSC) was performed on a Discovery DSC from TA Instruments. The thermal analyses were performed at a heating and

cooling rate of 10°C/min. Glass transition temperatures (T_g) were measured at the inflection point. The mechanical properties of the membranes were tested with Electroforce (EF) 3200 series from TA instrument with displacement ratio of 2.2 mm/min. The extractables from the crosslinked membranes were measured by Soxhlet extraction with ethanol and calculated by use of eq. 1).[12] The thickness of the membranes were measured with a Digitix II thickness gauge from NSK. At least 10 points were measured for every membrane; the average value was calculated and used as the membrane thickness.

$$X(\text{Soxhlet})(\%) = \text{Gel} - \text{content} = \left(\frac{M_2}{M_1} \right) \cdot 100, M_2 \leq M_1 \quad 1)$$

2.5 Gas permeation experiment

The single gas permeability (P) and diffusivity coefficient (D) of all the membranes were measured using a time-lag apparatus. A detailed description of the apparatus has been published elsewhere.[13] All the measurements took place at room temperature with the upstream pressure of 2 bar and the downstream pressure of approximately 0.04 mbar. The mechanism for gas transporting through polymer membranes is known to follow a solution-diffusion mechanism. The relationship of P (Barrer= $10^{-10} \text{ cm}^3 \text{ (STP) cm s}^{-1} \text{ cm}^{-2} \text{ cm Hg}^{-1}$), diffusivity (D) ($\text{cm}^2 \text{ s}^{-1}$) and solubility (S) ($\text{cm}^3 \text{ (STP) cm}^{-3} \text{ cm Hg}^{-1}$) of the gas in the polymer membrane is described in eq. 2). [10]

$$P = S \times D \quad 2)$$

The single gas diffusivity coefficient can be calculated from the eq. 3), in which “ l ” represents the thickness of the membrane and “ θ ” represents “time-lag”.

$$D = \frac{l^2}{6\theta} \quad 3)$$

The ideal selectivity, $\alpha_{i/j}$, was calculated by the ratio of species permeability, shown as eq. 4):

$$\alpha_{i/j} = \frac{P_i}{P_j} \quad 4)$$

3. Result and discussion

3.1 Synthesis of poly(VIm-co-BuA)

Imidazoles are popular for preparation of RTILs, since these are easily converted into a range of ILs by reaction with a broad selection of alkyl halides. Correspondingly, poly(RTILs) can easily be prepared by use of VIm based RTIL monomer, which polymerizes through free radical and controlled radical conditions. Poly(VIm) is a semicrystalline polymer, which is extremely brittle, which limits its application in many fields. It is also not possible to form free standing membranes consisting solely of poly(VIm) due to this brittleness. It was recently shown that direct 3D printing of mixtures of VIm and BuA result in a material with a significantly reduced brittleness[14]. Since, the copolymer composition from free radical copolymerization of BuA and VIm in solution has not been investigated, the copolymer reactivity ratios were determined by preparation of a range of different copolymers from different feed compositions. The structure of the prepared polymers was confirmed with FT-IR and ¹H NMR. The FT-IR spectra of poly(VIm), in Fig. 1, exhibits the characteristic peaks of VIm, C=C-H and N=C-H stretching at 3111cm⁻¹ and 1494 cm⁻¹, C=N stretching at 1660 cm⁻¹, ring vibrations at 1282 and 1230 cm⁻¹, CH out-of-plane bending at 914 cm⁻¹, ring torsion at 662 cm⁻¹ and C=C-H and N=C-H wagging at 634 cm⁻¹. Moreover, the characteristic peaks of poly(BuA) are also shown in Fig. 1, the peaks range of 3011-2827 cm⁻¹, at 1451cm⁻¹ and 1381cm⁻¹represent the C-H of methyl and methylene groups symmetric and asymmetric stretching. The peaks at 1727 cm⁻¹and 1154 cm⁻¹ are related to stretching vibration of C=O and C-O-C in acrylate group. The poly(VIm-co-BuA) FT-IR spectra shows peaks from both poly(VIm) and poly(BuA), though the intensity of peaks originating from VIm are generally weaker than the peaks from poly(BuA). The hygroscopicity of PVIm [15] results in traces of water being observed in both IR spectra, even though the samples were dried prior to analysis.

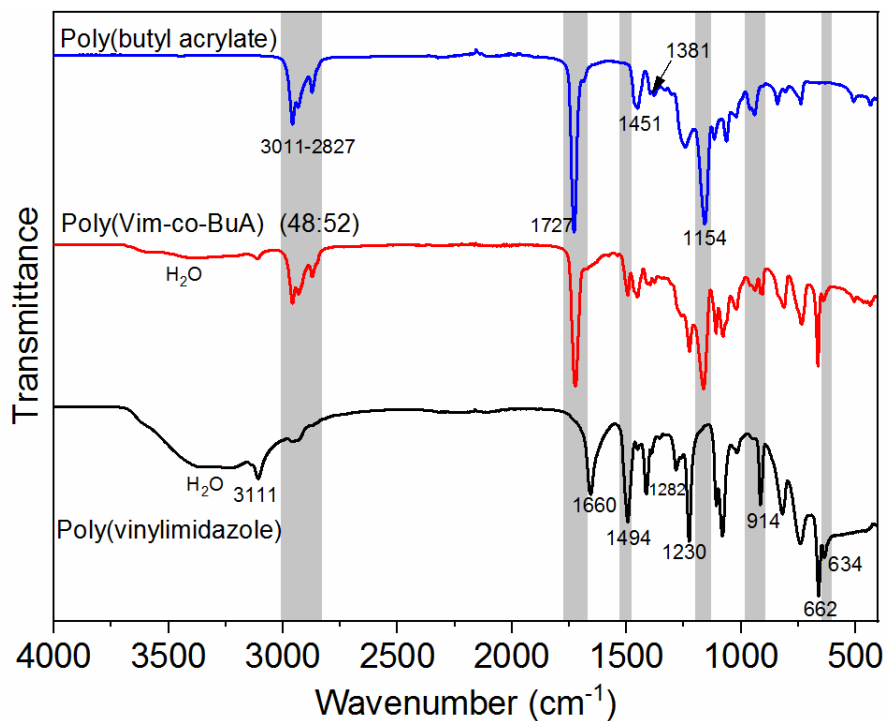


Fig. 1 The FT-IR spectra of poly(VIm), poly(VIm-co-BuA) (48:52) and poly(BuA).

The molar composition of the copolymer was calculated from ^1H NMR, where the molar fraction of VIm was determined from the integration of the imidazole protons at δ_{H} 7.4-6.4 ppm relative to the methylene protons (δ_{H} 4.1-3.5 ppm) in BuA (as shown in Fig. 2). For instance, the molar fraction of VIm in poly(VIm-co-BuA) prepared from a feed composition of 50:50 VIm:BuA is 48 mol%.

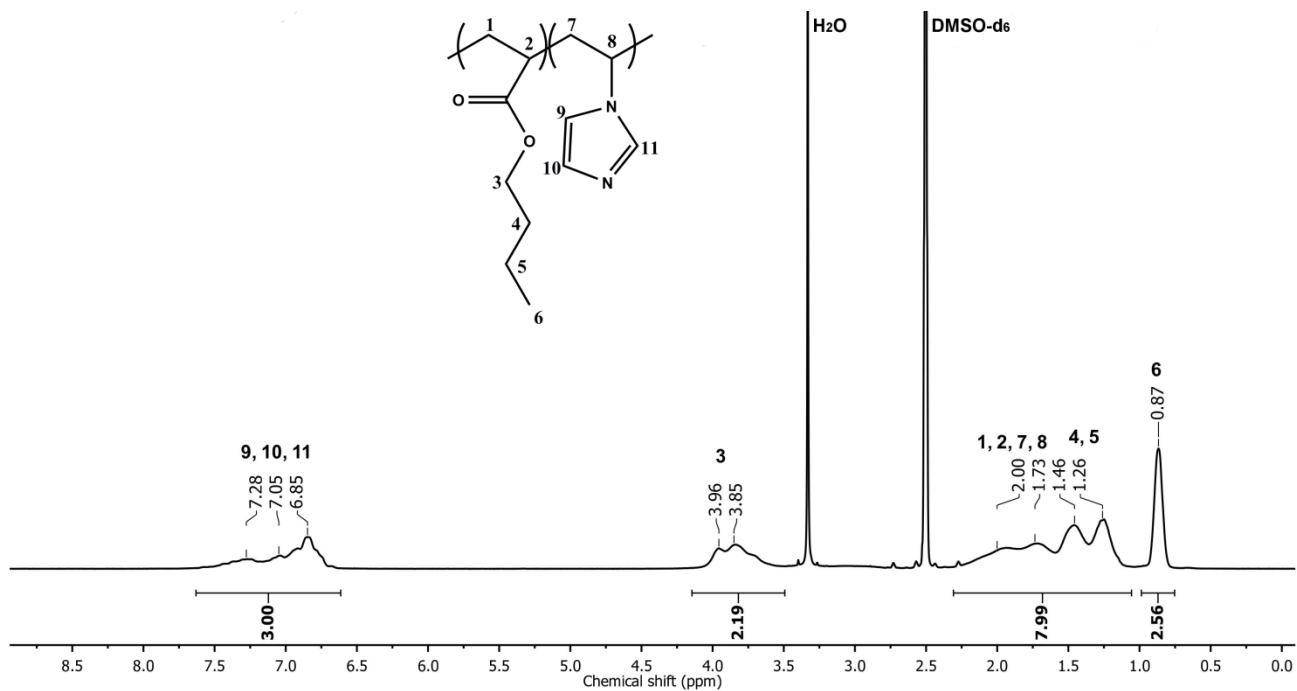


Fig. 2 ¹H NMR spectrum of poly(VIm-co-BuA) (48:52) run in DMSO-*d*₆.

The reactivity ratios were determined based on a series of copolymerizations of BuA and VIm with 10, 30, 50, 70 and 90 mol% BuA, which were terminated at low conversion to ensure constant feed composition. From ¹H NMR of the initially formed products of poly(VIm-co-BuA), the copolymer content of BuA (F₁) and VIm (F₂) could be determined. Based on a non-linear least squares (NLLSQ) fit and the method of Kelen and Tüdös,[16][17] the copolymer reactivity ratios were calculated as shown in Fig. 3.

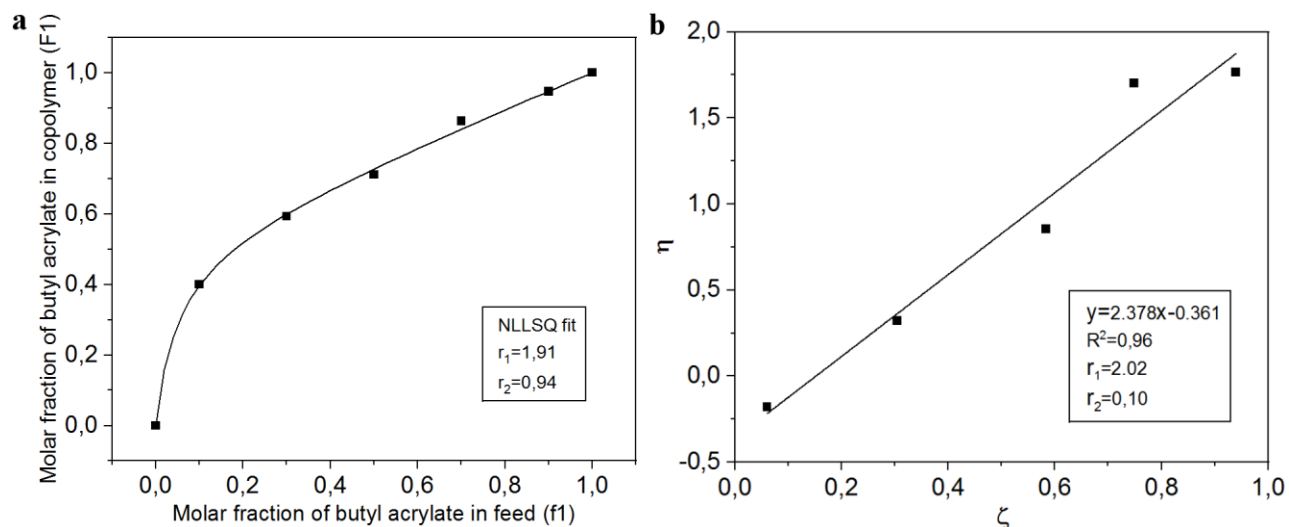


Fig. 3: a) Poly(VIm-co-BuA) composition diagram and NLLSQ fit. b) Kelen-Tüdös plot of poly(VIm-co-BuA)

The molar fraction of BuA in the feed (f_1) versus that in the copolymer (F_1) (shown in Fig. 3 (a)), shows a clear deviation from ideal copolymerization. The initially formed copolymer will have a higher content of BuA relative to VIm compared to the feed ratio. This is directly reflected in the reactivity ratios determined by the NLLSQ fit ($r_{\text{BuA}}=1.91$ and $r_{\text{VIm}}=0.094$) and by the method of Kelen and Tüdös ($r_{\text{BuA}}=2.02$ and $r_{\text{VIm}}=0.10$) for BuA and VIm, respectively. Even though these reactivity ratios deviate from ideal copolymerization, it is possible to obtain copolymers containing both repeating units in reasonable amounts.

A range of different copolymers of VIm and BuA was therefore prepared to determine the optimal copolymer compositions for preparation of free standing membranes with a high VIm content and a sufficient flexibility. The physical appearance of the prepared polymers is shown in the supporting information, SI-Fig 10. The polymers have an amphiphilic nature, which unfortunately prevents SEC analysis of the compositions with more than 24 mol% VIm in the copolymer (SEC in both THF and salted DMF has been tried). SEC of the 24 mol% VIm copolymer displays only a single peak, corroborating that a true copolymerization took place (supporting information SI-Fig 9). Thermal characterization of the copolymers was conducted by TGA and DSC (see Figure 4).

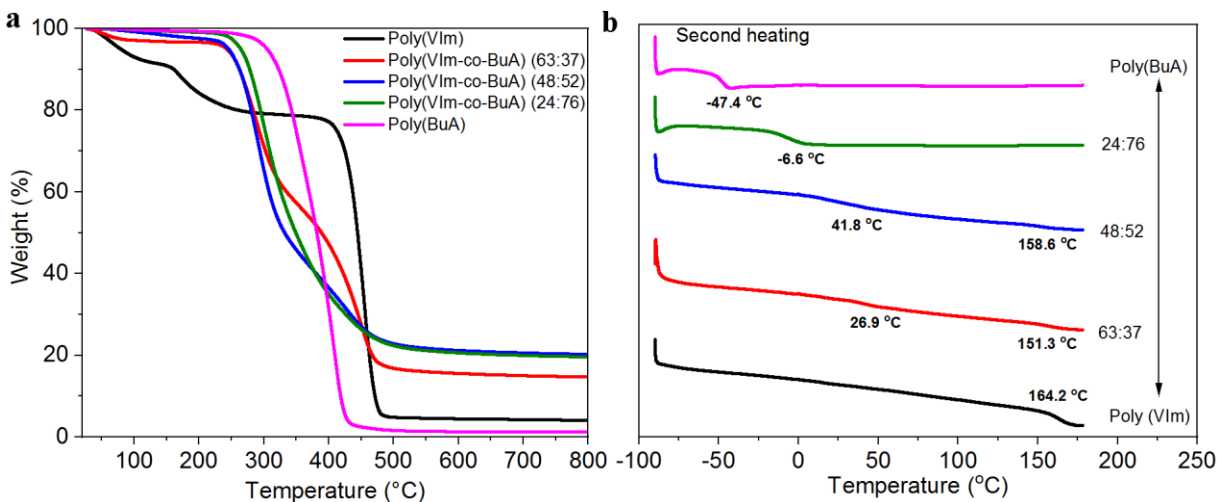


Fig. 4 Thermogravimetric analysis (a) and DSC thermograms showing second heating cycle (b) of poly(VIm), poly(BuA) and copolymers with different composition.

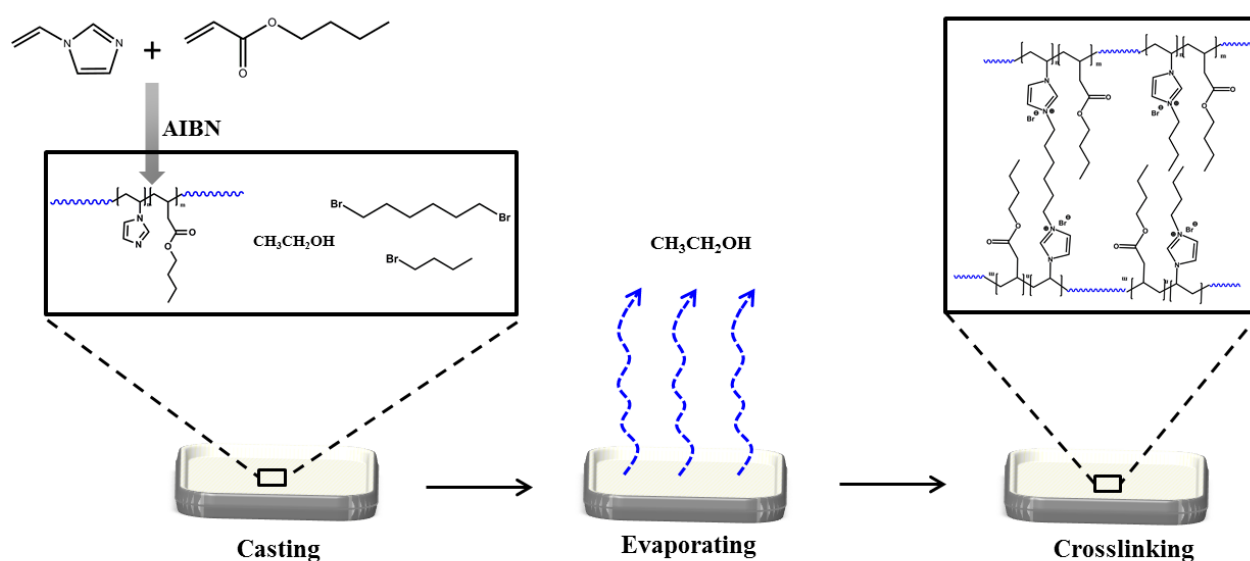
The TGA analysis (shown in Fig. 4(a)) illustrates the hygroscopic nature of poly(VIm), where there is a very clear weight loss of water in the initial phase of the analysis for the homopolymer of Poly(VIm). With incorporation of BuA in the copolymers, this is reduced, though there is a minor weight loss observed, in-line with the amount of VIm in the copolymers. The thermal degradation of all the copolymers takes place in a two-step behaviour, reflecting the content of the two monomers, and for all of the copolymers it is initiated at a lower temperature compared to the pure homopolymers (Poly(VIm) or Poly(BuA)), though this is still sufficiently high to permit application in gas-membranes.

The introduction of BuA provided the required flexibility for the copolymers (see DSC thermograms in Figure 4(b)). An interesting detail can be seen from the first heating curve in the DSC analysis (supporting information SI-Fig 11), where the absorbed water results in an evaporation. After evaporation of the water, one glass transition (T_g) is observed for the homopolymers (-47.2 °C for Poly(BuA) and 164 °C for Poly(VIm)), while the copolymers show intermediate glass transition temperatures. For the two systems with a high content of VIm (48 and 63 mol%), two thermal transitions can be observed 26.9 °C and 151.3 °C as well as 41.8 °C and 158.6 °C, respectively. This could indicate formation of free Poly(VIm) or formation of a tapered copolymer (though this cannot be confirmed without SEC analysis). From all the prepared copolymers, poly(VIm-co-BuA) with ratio of 24:76 has the most

interesting combination of a sufficiently high content of VIm, while still exhibiting a low glass transition temperature, ultimately resulting in a flexible material.

3.2 Preparation of free-standing poly(VIm-co-BuA) membranes

Poly(RTIL) membranes were prepared from the 24:76 VIm:BuA copolymer (poly(VIm-co-BuA)) by direct one-pot solvent casting and crosslinking using mixtures of 1, 6-dibromohexane and 1-bromobutane as shown in Scheme 1.



Scheme 1 Copolymer preparation and one-pot casting and crosslinking of membranes.

The simultaneous crosslinking and functionalization reaction resulted in free-standing membranes, where reaction of the VIm repeating units leads to the highest possible amount of poly(RTIL) in each membrane. Four kinds of membranes were prepared in this work, the so-called 20 %, 50 % and 100 % crosslinked membranes have been prepared using a 1:8, 1:2 or a 1:0 ratio of 1, 6-dibromohexane to 1-bromobutane. By varying the ratio between cross-linker (1,6-bromo-hexane) and blocking agent (1-bromobutane), membranes with different crosslinking degree were obtained, while maintaining a similar IL character.

Any unreacted blocking agent or cross-linker was removed by evacuation after crosslinking, resulting in membranes with a low soluble fraction (<10%) and very high gel fractions (> 90%), as shown in Table 1. In addition to free standing poly(RTIL) membranes, it was also possible to add additional free IL, in order to assess the possibility to increase the affinity for CO₂. The membrane with free IL could be prepared with up to 16 wt% IL. Higher amounts of free IL hindered the crosslinking reaction and could therefore not be prepared.

There is no obvious difference observed in the FT-IR spectra of membranes with different crosslinking degree (shown in Fig. 5 (a)), since these membranes are effectively chemically equivalent. Fig. 5 (b) shows the FT-IR spectra of the 100 % crosslinked membrane, 100 % crosslinked membrane with free ionic liquid BMIM Tf₂N and the ionic liquid, BMIM Tf₂N. It can be seen that the peaks of 100 % crosslinked membrane with free ionic liquid is the combination of that of BMIM Tf₂N and 100 % crosslinked membrane. Additionally, there is no shift of the peaks, indicating that there are no chemical interaction between the membrane network and the ionic liquid.

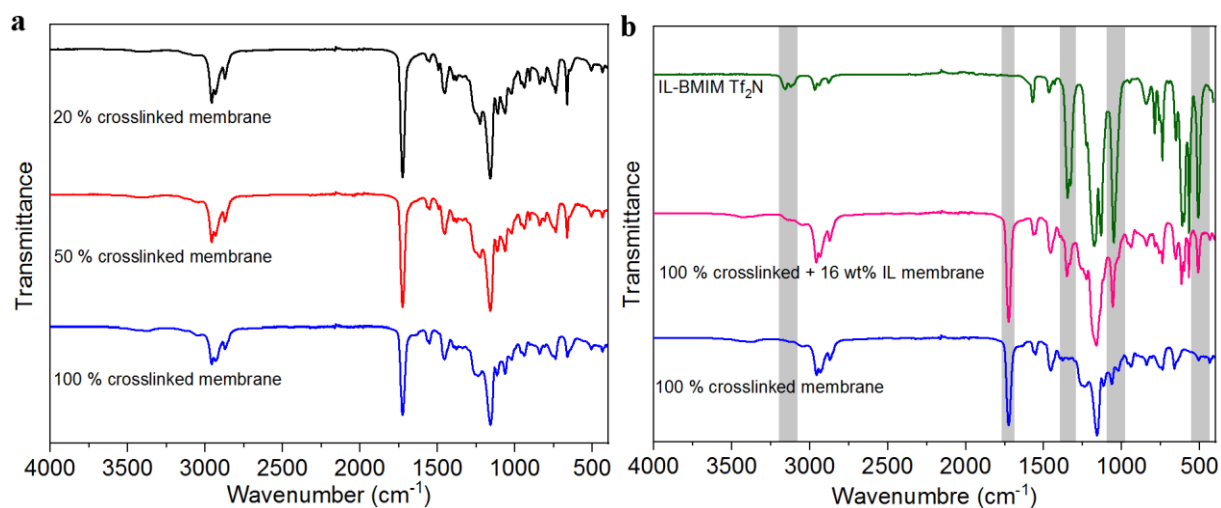


Fig. 5 FT-IR spectra of all the prepared membranes with 20, 50 and 100 % crosslinker (a) as well as the 100 % crosslinked membrane with free ionic liquid and the ionic liquid BMIM Tf₂N (b).

3.3 Thermal properties

Thermogravimetric analysis of the membranes (see Figure 6) show an even further decreased onset of decomposition for the membranes compared to that of poly(VIm-co-BuA), which decreased from 268°C to 220°C

after crosslinking. This is ascribed to protonation with a hydrogen halide, which has been observed in other cases for poly(RTIL)s.[14] For the membranes, the first stage of weight loss is observed between 220-350 °C corresponding to decomposition of the cross linker and the acrylate part of the polymer backbone; while the second degradation between 350-530 °C is attributed to decomposition of the imidazole ring and the polymer backbone, as has also been observed in other imidazole systems.[18] The residue after thermal degradation is constant for all the membranes, indicating that this relates to the copolymer composition and not the crosslinker/butyl bromide ratio. In the case of additional free IL, this residue is reduced corresponding to the 16 wt% of IL. The thermal stability of the all membranes is concluded to be sufficient for these materials to be applicable for gas separation membranes, where temperatures between 25-75 °C of representative flue gas are expected.[19]

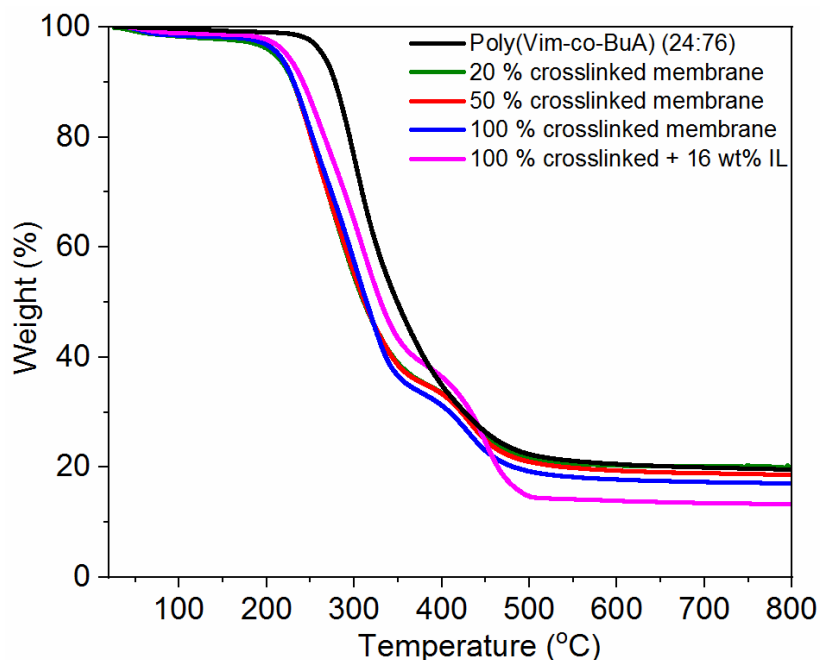


Fig. 6 TGA of poly(VIm-co-BuA) (24:76) and all the prepared membranes.

The thermal properties of the crosslinked membranes were also investigated by DSC (SI-Fig 17-20). From the first heating curve in the DSC analysis of the membranes, evaporation of water can be seen in all of the membranes, which is attributed to the **hygroscopic nature of systems containing VIm**. However, on the second heating curve, it is not possible to identify glass transition temperatures for any of the membranes. Crosslinking of the membranes

was expected to result in a minor increase in glass transition temperature compared to the original copolymer, as is well known from other curing reactions.[20] All of the membranes appear soft and flexible, which indicate that the apparent glass transition temperatures is below RT (see picture of films in the supporting information SI-Fig 21). This can either be a result of an actual low glass transition temperature, or a result of water plasticizing the crosslinked membranes.

3.4 Mechanical property of crosslinked poly(VIm-co-BuA) membrane

The mechanical properties of the membranes were evaluated by tensile testing. The stress-strain curve of the membranes is shown in supporting information SI-Fig 27. Young's modulus (MPa), Tensile strength (MPa) and elongation at break (%) for the membranes are summarized in Table 1.

Table 1 Gel fraction and mechanical properties of membranes.

	Gel fraction (%)	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
20 %	95.77 ± 0.1	0.0015	0.024	>53
50 %	97.39 ± 0.39	0.0135	0.061	>53
100 %	98.41 ± 0.03	0.0395	0.11	29.8
100 % + 16 wt% IL	85.35 ± 0.18	0.0034	0.056	39.2

Young's modulus was determined from the slope of the stress–strain curve, and it clearly increases with increasing degree of crosslinking. In addition, Young's modulus of the membrane with IL is observed to be between that of the 20 % and 50 % crosslinked membranes, because of the plasticizing effect. The 100 % crosslinked membrane and 100 % crosslinked membrane with 16 wt% IL showed elongations at break of 29.8% and 39.2 %, respectively. However, the less crosslinked systems could not be extended to their breaking points due to instrument limitations, resulting in extensions at break above 53%. All of the membranes exhibit mechanical properties that enable them to be used for gas-phase membranes.

3.5 Gas permeation properties

The gas separation performances of all the membranes were evaluated with a single gas apparatus. The permeability of CO₂, N₂ and CH₄ and permselectivities of CO₂/N₂ and CO₂/CH₄ are listed in Table 2. In another study by Gabriel Zarca et al.,[21] the CO₂ permeability of a supported poly[C₄vim] [Tf₂N⁻] membrane has been observed to be 5.2 Barrer with CO₂/N₂ permselectivities of 17.3. The CO₂ permeability of membranes prepared in this work ranges from 33.71 to 54.38, which increased about 6.5 to 10.5 times, and CO₂/N₂ permselectivities of more than 20, even though Tf₂N⁻ counterions are known to have significantly higher CO₂-philicity than halogen ions. The increased CO₂ permeability is attributed to the introduction of BuA, which leads to a much lower glass transition temperature of the membranes. At the same time, it also gave higher fractional free volume, which is known to be beneficial for gas transportation. [22][23] Additionally, the oxygen in the acrylate ester group and its ability to interact with CO₂,[24] could also be an explanation for the improvement of CO₂ permeability.

Table 2 The permeability of CO₂, N₂ and CH₄ and permselectivities of CO₂/N₂ and CO₂/CH₄.

Membrane	Permeability (Barrer)			Permselectivity	
	CO ₂	N ₂	CH ₄	α_{CO_2/N_2}	α_{CO_2/CH_4}
20 %	54.38	11.79	6.16	4.61	8.83
50 %	44.35	2.05	5.16	21.63	8.59
100 %	33.71	1.62	3.64	20.81	9.19
100 % + 16 wt% IL	38.77	1.39	4.18	27.82	9.28

3.5.1 Membranes with different degrees of crosslinking

The gas separation performance of membranes with different degrees of crosslinking, 20 %, 50 % and 100 %, was investigated. Table 2 shows that the gas permeability increases with decreasing of degree of crosslinking. From the degree of crosslinking of 100 % to 50 %, the permeability of CO₂ increased from 33.71 to 44.35 Barrer without compromising the permselectivity. This may be explained by the lower degree of crosslinking providing increasing free-volume for the transportation of gases, which is consistent with results of other systems.[25]

Additionally, the increase of CO₂ permeability is higher than that of N₂ and CH₄, which illustrates that the poly(RTIL) membranes have better affinity to CO₂. The observed difference in mechanical properties and lower degree of crosslinking in the 20 % crosslinked membrane leads to a considerably more open structure, resulting in an increased permeability and diffusivity of N₂, as shown in Table 2 and 3, respectively.

Table 3 The diffusivity and solubility of CO₂, N₂ and CH₄ in the crosslinked poly(VIm-co-BuA) membranes.

Membrane	Diffusivity ($\times 10^7 \text{ cm}^2 \text{ s}^{-1}$)			Solubility ($\text{cm}^3(\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$)		
	CO ₂	N ₂	CH ₄	CO ₂	N ₂	CH ₄
20 %	1.95	2.42	1.91	2.12	0.37	0.25
50 %	1.82	1.90	2.21	1.85	0.082	0.18
100 %	1.44	N/A	1.49	1.78	N/A	0.19
100 % + 16 wt% IL	1.95	N/A	1.57	1.51	N/A	0.20

N/A: time-lag could not be accurately determined due to very slow permeation rate.

3.5.2 Composite membrane with free IL

Based on previous investigations, introduction of free ionic liquid is an efficient way to improve the CO₂ separation performance of poly(IL) membranes.[10][26] In this work, 16 wt% BMIM Tf₂N was added to the 100 % crosslinked membrane. Table 2 and 3 show gas separation behaviors of membranes before and after the addition of free IL. The gas permeability and permselectivity of the membrane with free IL increased as expected. At the same time, the diffusivity coefficient increased from 1.44 to $1.95 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$ and the solubility coefficient decreased from 1.78 to $1.51 \text{ cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$. This illustrates that the increased permeability is a result of the added RTIL acting as a plasticizer of the poly(RTIL) membrane, and not a result of increased CO₂ solubility, due to the high CO₂ solubility of free RTIL.

4 Conclusion

A series of copolymer poly(VIm-co-BuA) were synthesized in the work. Poly(VIm-co-BuA) (24:76) was found to be the best compromise between amount of VIm and thermal properties ($T_g = -6.8 \text{ }^\circ\text{C}$), and it was therefore used for preparation of free-standing poly(RTILs) membranes. Membranes were prepared by crosslinking

poly(VIm-co-BuA) with a combination of 1, 6-dibromohexane (cross linker) and 1-bromobutane (blocker). The gas separation performance was directly correlated to the degree of crosslinking, where CO₂ permeability was increased from 33.7 Barrer for the 100 % crosslinked membrane to 54.4 Barrer for the 20 % crosslinked membrane. However, the more flexible 20 % crosslinked membrane also showed a significantly increased permeability of N₂. An optimal balance between permeability and selectivity was observed for the 50% crosslinked membrane, which showed both a high permeability to CO₂ (44.4 Barrer) as well as a good permselectivity of CO₂ over N₂ of 21.2. An ion gel was also prepared in this work by introducing 16 wt% free IL BMIM Tf₂N in the 100 % crosslinked membrane, showing increased CO₂ permeability from 33.71 to 38.77 Barrer and increased permselectivity of CO₂/N₂ from 20.81 to 27.82.

The results showed that the crosslinked membranes have potential to separate CO₂ from flue gas and natural gas. Compared to the analogous neat poly(RTIL) membranes, both the permeability of CO₂ and the permselectivity of CO₂/N₂ were increased.

Acknowledgement

References

- [1] S.P.M. Ventura, F.A. e Silva, M. V Quental, D. Mondal, M.G. Freire, J.A.P. Coutinho, Ionic-Liquid-Mediated Extraction and Separation Processes for Bioactive Compounds: Past, Present, and Future Trends, *Chem. Rev.* 117 (2017) 6984–7052. doi:10.1021/acs.chemrev.6b00550.
- [2] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Ionic-liquid materials for the electrochemical challenges of the future, *Nat. Mater.* 8 (2009) 621–629. doi:10.1038/nmat2448.
- [3] W. Zhao, Y. Tang, J. Xi, J. Kong, Functionalized graphene sheets with poly(ionic liquid)s and high adsorption capacity of anionic dyes, *Appl. Surf. Sci.* 326 (2015) 276–284. doi:10.1016/j.apsusc.2014.11.069.

- [4] A.M. Lopez, M.G. Cowan, D.L. Gin, R.D. Noble, Phosphonium-Based Poly(ionic liquid)/Ionic Liquid Ion Gel Membranes: Influence of Structure and Ionic Liquid Loading on Ion Conductivity and Light Gas Separation Performance, *J. Chem. Eng. Data.* (2018) acs.jced.7b00541. doi:10.1021/acs.jced.7b00541.
- [5] D.B. Wijayasekara, M.G. Cowan, J.T. Lewis, D.L. Gin, R.D. Noble, T.S. Bailey, Elastic free-standing RTIL composite membranes for CO₂/N₂ separation based on sphere-forming triblock/diblock copolymer blends, *J. Memb. Sci.* 511 (2016) 170–179. doi:10.1016/j.memsci.2016.03.045.
- [6] J.L. Anthony, E.J. Maginn, J.F. Brennecke, Solubilities and thermodynamic properties of gases in the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate, *J. Phys. Chem. B.* 106 (2002) 7315–7320. doi:10.1021/jp020631a.
- [7] P. Scovazzo, J. Kieft, D.A. Finan, C. Koval, D. DuBois, R. Noble, Gas separations using non-hexafluorophosphate [PF₆]- anion supported ionic liquid membranes, *J. Memb. Sci.* 238 (2004) 57–63. doi:10.1016/j.memsci.2004.02.033.
- [8] R.M. Teodoro, L.C. Tomé, D. Mantione, D. Mecerreyes, I.M. Marrucho, Mixing poly(ionic liquid)s and ionic liquids with different cyano anions: Membrane forming ability and CO₂/N₂ separation properties, *J. Memb. Sci.* 552 (2018) 341–348. doi:10.1016/j.memsci.2018.02.019.
- [9] J.E. Bara, S. Lessmann, C.J. Gabriel, E.S. Hatakeyama, R.D. Noble, D.L. Gin, Synthesis and Performance of Polymerizable Room-Temperature Ionic Liquids as Gas Separation Membranes, *Ind. Eng. Chem. Res.* 46 (2007) 5397–5404. doi:10.1021/ie0704492.
- [10] T.K. Carlisle, E.F. Wiesenauer, G.D. Nicodemus, D.L. Gin, R.D. Noble, Ideal CO₂ /Light Gas Separation Performance of Poly(vinylimidazolium) Membranes and Poly(vinylimidazolium)-Ionic Liquid Composite Films, *Ind. Eng. Chem. Res.* 52 (2013) 1023–1032. doi:10.1021/ie202305m.
- [11] J.E. Bara, R.D. Noble, D.L. Gin, Effect of “Free” Cation Substituent on Gas Separation Performance of

- Polymer–Room-Temperature Ionic Liquid Composite Membranes, *Ind. Eng. Chem. Res.* 48 (2009) 4607–4610. doi:10.1021/ie801897r.
- [12] C. Hirschl, L. Neumaier, S. Puchberger, W. Mühleisen, G. Oreski, G.C. Eder, R. Frank, M. Tranitz, M. Schoppa, M. Wendt, N. Bogdanski, A. Plösch, M. Kraft, Determination of the degree of ethylene vinyl acetate crosslinking via Soxhlet extraction: Gold standard or pitfall?, *Sol. Energy Mater. Sol. Cells.* 143 (2015) 494–502. doi:10.1016/j.solmat.2015.07.043.
- [13] Z. Dai, L. Ansaloni, D.L. Gin, R.D. Noble, L. Deng, Facile fabrication of CO₂ separation membranes by cross-linking of poly(ethylene glycol) diglycidyl ether with a diamine and a polyamine-based ionic liquid, *J. Memb. Sci.* 523 (2017) 551–560. doi:10.1016/j.memsci.2016.10.026.
- [14] E. Karjalainen, D.J. Wales, D.H.A.T. Gunasekera, J. Dupont, P. Licence, R.D. Wildman, V. Sans, Tunable Ionic Control of Polymeric Films for Inkjet Based 3D Printing, *ACS Sustain. Chem. Eng.* 6 (2018) 3984–3991. doi:10.1021/acssuschemeng.7b04279.
- [15] H.M.L. Thijs, C.R. Becer, C. Guerrero-Sanchez, D. Fournier, R. Hoogenboom, U.S. Schubert, Water uptake of hydrophilic polymers determined by a thermal gravimetric analyzer with a controlled humidity chamber, *J. Mater. Chem.* 17 (2007) 4864–4871. doi:10.1039/b711990a.
- [16] T. Kelen, F. Tüdös, Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method, *J. Macromol. Sci. Part A - Chem.* 9 (1975) 1–27. doi:10.1080/00222337508068644.
- [17] J.P. Kennedy, T. Kelen, F. Tüdös, Analysis of the linear methods for determining copolymerization reactivity ratios. II. A critical reexamination of cationic monomer reactivity ratios, *J. Polym. Sci. Polym. Chem. Ed.* 13 (1975) 2277–2289. doi:10.1002/pol.1975.170131010.
- [18] T. Feng, B. Lin, S. Zhang, N. Yuan, F. Chu, M.A. Hickner, C. Wang, L. Zhu, J. Ding, Imidazolium-based

- organic–inorganic hybrid anion exchange membranes for fuel cell applications, *J. Memb. Sci.* 508 (2016) 7–14. doi:10.1016/j.memsci.2016.02.019.
- [19] A. Sayari, Y. Belmabkhout, R. Serna-Guerrero, Flue gas treatment via CO₂ adsorption, *Chem. Eng. J.* 171 (2011) 760–774. doi:10.1016/j.cej.2011.02.007.
- [20] H.D. Nguyen, D. Löf, S. Hvilsted, A.E. Daugaard, Highly branched bio-based unsaturated polyesters by enzymatic polymerization, *Polymers (Basel)*. 8 (2016) 363. doi:10.3390/polym8100363.
- [21] G. Zarca, W.J. Horne, I. Ortiz, A. Urriaga, J.E. Bara, Synthesis and gas separation properties of poly(ionic liquid)-ionic liquid composite membranes containing a copper salt, *J. Memb. Sci.* 515 (2016) 109–114. doi:10.1016/j.memsci.2016.05.045.
- [22] F.F. Csikor, C. Motz, D. Weygand, M. Zaiser, S. Zapperi, Dislocation avalanches, strain bursts, and the problem of plastic forming at the micrometer scale, *Science* (80-.). 318 (2007) 251–254. doi:10.1126/science.1143719.
- [23] H. Lin, E. Van Wagner, R. Raharjo, B.D. Freeman, I. Roman, High-performance polymer membranes for natural-gas sweetening, *Adv. Mater.* 18 (2006) 39–44. doi:10.1002/adma.200501409.
- [24] Z. Ma, Z. Qiao, Z. Wang, X. Cao, Y. He, J. Wang, S. Wang, CO₂ separation enhancement of the membrane by modifying the polymer with a small molecule containing amine and ester groups, *RSC Adv.* 4 (2014) 21313. doi:10.1039/c4ra01107d.
- [25] X. Zhou, M.M. Obadia, S.R. Venna, E.A. Roth, A. Serghei, D.R. Luebke, C. Myers, Z. Chang, R. Enick, E. Drockenmuller, H.B. Nulwala, Highly cross-linked polyether-based 1,2,3-triazolium ion conducting membranes with enhanced gas separation properties, *Eur. Polym. J.* 84 (2016) 65–76. doi:10.1016/j.eurpolymj.2016.09.001.

- [26] J.E. Bara, D.L. Gin, R.D. Noble, Effect of Anion on Gas Separation Performance of Polymer–Room-Temperature Ionic Liquid Composite Membranes, *Ind. Eng. Chem. Res.* 47 (2008) 9919–9924. doi:10.1021/ie801019x.