DTU Chemical Engineering

Department of Chemical and Biochemical Engineering

Poly(ionic liquid) membranes for CO_2 separation from N_2

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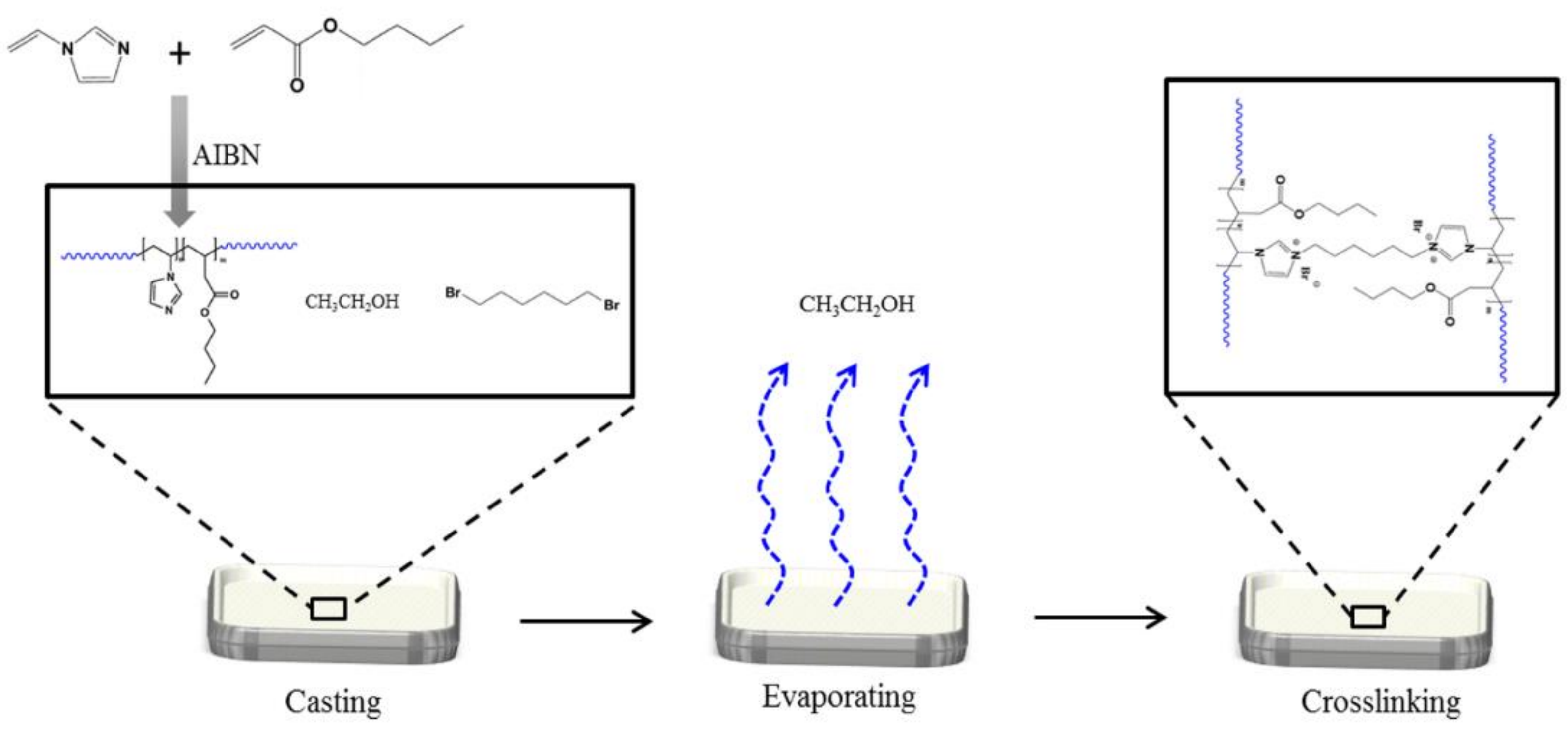
Introduction

Poly(vinylimidazole) is a semicrystal polymer, which is extremely brittle. The brittleness limits its applicability for free-standing membrane. In order to overcome the shortcoming of poly(Vim), a soft comonomer, butyl acrylate, was introduced in copolymerization with N-vinylimidazole.[1] Poly(Vim-co-BuA), which is relatively flexible, was synthesized through free radical polymerization with AIBN as initiator.

Subsequently, poly(Vim-co-BuA) was crosslinked with 1,6-dibromohexane, forming poly(ionic liquid) membranes. The membranes with different crosslinking degrees of 20 %, 50 % and 100 % and with 25 phr ionic liquid (IL) BMIM Tf_2N were prepared in this work. The membrane present potentials for CO_2 separation from N_2 and CH_4. The influence of crosslinking degree to gas separation were investigated. It turns out that CO_2 permeability increased with decreasing the degree of crosslinking. Additionally, the addition of free ionic liquid also lead to an improvement of the gas separation performance.

Experimental



Scheme 1 Process of membrane formation.

Thermal properties

Tg of the copolymer, poly(Vim-co-BuA), decreased down to -15.8 °C from 155.4 °C for poly(Vim) as rubbery polymer, It confirmed that the introduction of butyl acrylate gave poly(Vim) the required softness. Tg of the membranes increases with increasing the degree of crosslinking. Similarity, blending with free IL results in membrane with lower Tg compared to that of the corresponding membranes with similar degree of crosslinking illustrating that IL here act as plasticizer.

Table 1 The glass transition temperature (DSC) of poly(BuA), poly(Vim), poly(Vim-co-BuA) and different membranes.

	Poly(BuA)	Poly(Vim)	Poly(Vim-co-BuA)	20 %	50 %	100 %	100 % + 25 phr IL
Tg (°C)	-54.4	155.4	-15.8	-9.9	27.1	37.3	3.9

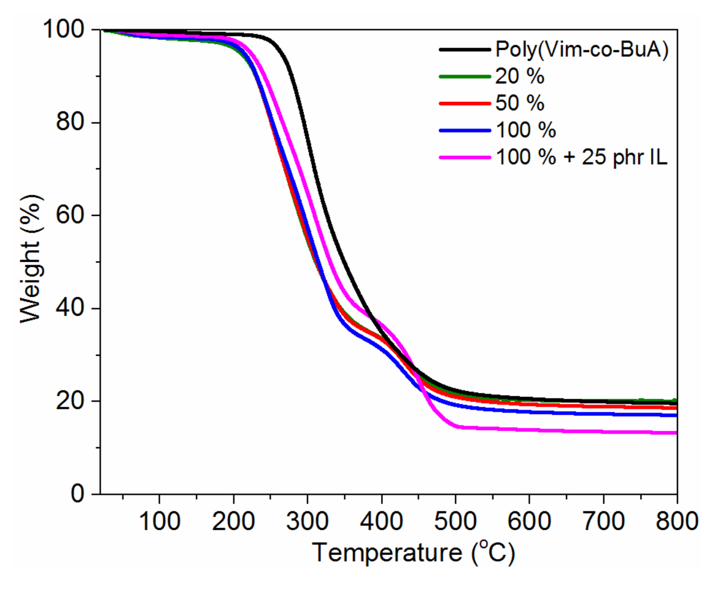


Figure. 1 TGA curve of poly(Vim-co-BuA) and all the prepared membranes

The onset decomposition temperature of the poly(Vim-co-BuA) decreases from 267.6 °C to around 220 °C after crosslinking, which is ascribed to the protonation with hydrogen halide.[1] The first staging of weight loss happened around 220-350 °C corresponded to the decomposition of cross linker and the butyl acrylate part of the polymer backbone;[2] The second degradation between 350-530 °C is contributed to the decomposition of the imidazole ring and polymer backbone.[3] In addition, because of the existence of free IL, the residue weight of the membrane with 25 phr IL is lower than the other membranes.

Mechanical properties

The Young's modulus of the membranes increased by increasing degree of crosslinking. The addition of ionic liquid also improved the flexibility of the membrane, which was consistent with the DSC result.

Table 2 Mechanical properties of the membranes

Membranes	Young's modulus (MPa)	Tensile strength at break (MPa)	Elongation at break (%)
20 %	0.0015	-	-
50 %	0.0135	-	-
100 %	0.0395	0.11	29.8
100 % + 25phr IL	0.0034	0.056	39.2

Gas separation properties

Membranes used for gas separation should have a favorable affinity to CO_2, so that CO_2 could preferentially pass through the membrane. (***Figure 1***)

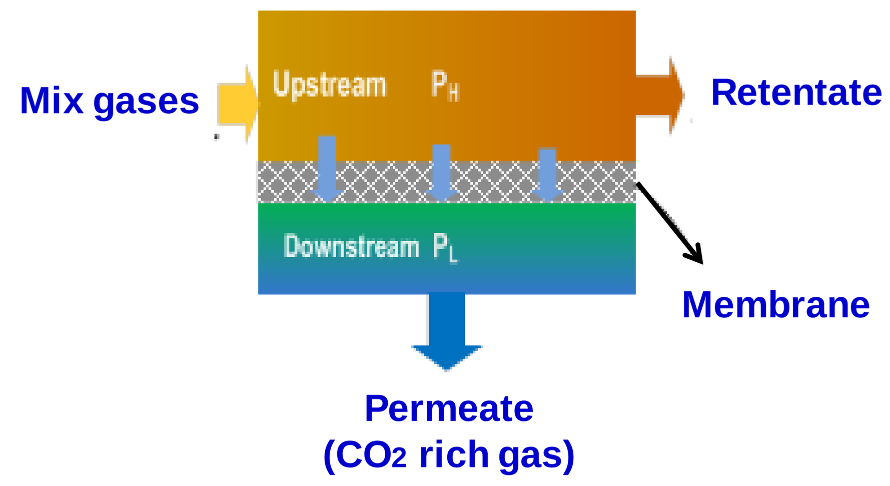


Figure 2. The mechanism of membrane gas separation.

Table 3 The permeability of CO_2, N_2 and CH_4 and permselectivities of CO_2/N_2 and CO_2/CH_4

Spacer	$P(CO_2)$	$P(N_2)$	$P(CH_4)$	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 % + 25 phr IL	38.77	1.39	4.18	27.82	9.28
Neat poly(Vim) based poly(IL) membrane[4]	5.2	0.3	-	17.3	-

Conclusions

- Poly(Vim-co-BuA) was synthesized trough free radical polymerization;
- Free-standing poly(IL) membranes were formed by crosslinking poly(Vim-co-BuA) with 1,6-dibromohexane;
- Membranes with different crosslinking degrees and with 25 phr IL were prepared and characterized with DSC, TGA and tension testing;
- Gas separation performance of the membranes was investigated, and it turns out that the poly(Vim-co-BuA) based membrane showed potential to gas separation.

Acknowledgment

We gratefully acknowledge use of the gas separation facilities in the Department of Chemical Engineering at Norwegian University of Science and Technology (NTNU).

References

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