

Imidazolium-Functionalized Poly(ether sulfone) as a Novel Polymeric Membrane for CO₂/CH₄ Separation

SHAOBO FU, TENG YANG ZHU, FEILONG PAN AND JUJIE LUO*

College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, China,

ABSTRACT

A series of novel gas separation membranes based on poly(ether sulfone)s were successfully synthesized via polycondensation, brominated and methyl imidazolium functionalization reactions. The structures and properties of this series, as well as the gas separation properties of the corresponding polymer membranes, were studied. The permeability and selectivity of the membranes were studied at different temperatures of 25-55°C and pressures of 0.5-1.5 atm, using single gases CO₂ and CH₄. Gas-permeation measurements showed that copolymers with different content of imidazolium ionic groups exhibited different separation performances. For example, the membrane from MIPESF-c showed better performance in terms of ideal selectivity over the other two copolymers membranes. The highest ideal CO₂/CH₄ selectivity was 34.5 with CO₂ permeability 18.5 barrer at 1.5 atm and 25°C.

KEYWORDS : Polysulfone, Imidazolium, Gas permeability, CO₂ Separation

INTRODUCTION

Global warming resulting from the increased CO₂ concentration in the atmosphere from fossil fuel combustion is becoming one of the most important environmental global issues^[1-6]. CO₂ capturing is critical process for environmental applications and for natural gas purification. Membrane-based gas separation is becoming increasingly important in various industries because of its low operation cost,

no phase transition, minimal energy requirements, ease of operation, and environmental friendliness^[7].

Thus, it is widely used in CO₂ separation area. Great efforts have been made to development of polymeric gas separation membranes in the last two decades^[8-12]. However, traditional polymers are based on solution-diffusion mechanism and can hardly breakthrough "Robeson up limit", so they are difficult to obtain

J. Polym. Mater. Vol. 34, No. 4, 2017, 719-732

© Prints Publications Pvt. Ltd.

Correspondence author e-mail: luojujie@126.com (Jujie Luo); zhutengyang@qq.com

high CO₂ permeation rate and selectivity. To obtain a membrane material that will overcome this limitation, many researchers have focused on facilitated transport (FT) membrane, which can break this limitation and get good permeation selectivity because of carriers in molecules. In FT membranes, the gas-transport behavior is dominated by the FT mechanism, which exploits the fast chemical reactions between CO₂ and basic compounds (also called “carriers”) at the feed gas/membrane interface to enhance CO₂ trans-membrane flux^[13].

Recently, a handful of studies have developed a new type of polymers in which pendant imidazolium-based ionic salts were introduced onto the polymer backbone as highly CO₂-selective polymer membranes. Membranes prepared from these newly developed polymers displayed high CO₂ separation and permeation properties by introducing imidazole carriers. Because imidazole groups have a strong interaction with CO₂, which could increase its solubility more than that with other gases. For example, Hong et al. prepared and characterized films from poly(vinyl chloride) (PVC) containing imidazolium pendant groups, a polymer rich in imidazole functionalities, and observed remarkable permeability and selectivity for separation of carbon dioxide. The best result of selectivity for CO₂/N₂ pair is 20.2 with 137.6 Barrer of permeability for CO₂^[14]. Jiang et al. reported the N₂ and CO₂ transport properties of polyphenylsulfones membranes containing imidazole group, for which the best value of CO₂/N₂ selectivity is 36.3 with 23.4 Barrer^[15]. For similar separations, Lodge et al. obtained new triblock copolymer membranes containing imidazolium groups for

gas separation. The results showed membranes exhibit excellent permeation performances for CO₂ and the CO₂/CH₄ permeation-separation performance of membrane with a 15 wt% content of imidazolium groups is near the upper-boundary^[16]. In another important work, Kim et al. synthesized and characterized a series of imidazolium-functionalized polyimides with a range of PEG chain lengths. The [C₁₂PEG-Im-PI][Br] membrane (the ethylene glycol chain lengths with C₁₂) showed better performance in terms of selectivity over the other copolymers membranes and the highest CO₂/CH₄ selectivity was achieved (49.2)^[17].

Based on the above design considerations, in this work, to enhance permeability to CO₂, imidazolium-functionalized poly(ether sulfone) containing fluorine group was synthesized via polycondensation, brominated, methyl imidazolium functionalization. A series of FT membranes were fabricated by changing the content of imidazolium. The permeability and selectivity of the synthesized polymers were fully investigated.

2. EXPERIMENTAL

Materials

All the chemicals are reagent grade and purified by standard methods. 2, 2-bis(4-hydroxyphenyl) hexafluoropropane (BPAF), 3, 3', 5, 5' -tetramethyl-4, 4'-dihydroxybiphenyl (TMBP, 99%), N-bromobutanamide (NBS) and bis(4-fluorophenyl)sulphone (BFPS) were purchased from Aldrich Reagent-grade. N-Methyl pyrrolidone (NMP), N, N'-dimethyl acetamide (DMAc), chloroform, methanol, ethyl acetate, acetone, 1-methylimidazole toluene, and calcium carbonate (Ca₂CO₃) were obtained from commercial sources. Toluene was dried over sodium wire prior to use.

Calcium carbonate was vacuum dried at 180°C for 10 h before use. Other reagents and solvents were used as received. CH₄ and CO₂ gases with purity of 99.99% were obtained from Gas Production Plant, Taiyuan (China).

Synthesis of poly(ether sulfone) (PESF)

As shown in Scheme 1, Poly(ether sulfone)(PESF) were prepared by polycondensation reaction with a stoichiometric ratio of various monomers, 1.3 equiv of potassium carbonate, NMP as the solvent, and toluene as the azeotropic agent. A typical procedure for the synthesis of the copolymers is as follows: 1.2116g(5mmol) of TMBP, 1.6812g(5mmol) of BPAF, 2.5431g(10mmol) of BFPS and 1.7967g(13mmol) of K₂CO₃ were added to a three-necked round bottom flask equipped with a magnetic stirrer, a nitrogen inlet, and a Dean-Stark trap. NMP(20 mL) was introduced to afford a 27.2 % (w/v) solid concentration. Toluene (10 mL, usually NMP/toluene = 2/1, v/v) was used as an azeotroping agent. Under the protection of nitrogen atmosphere, the reaction mixture was refluxed at 145°C for 3 h to dehydrate the system. After the removal of toluene, the temperature was slowly increased to 185°C and kept for 8 h. After the solution became very viscous, the reaction mixture was cooled to 80°C, diluted with the addition of 20 mL NMP and poured into 300 mL stirred water to precipitate the product. The precipitate was filtered and washed several times with water to remove inorganic salts. Finally, it was vacuum dried at 80°C for 24 h. An amount of 5.2485g PESF was obtained in high yield of 96%.The molecular feed ratio of monomers and the polymerization result were list in Table 1.

Preparation of bromide poly(ether sulfone)s (BPESFs)

A typical procedure of bromination reaction of poly(ether sulfone) was as follows: PESF(30 mmol) was dissolved in 200mL chloroform at 30°C. To the clear solution 60 mmol of NBS and 4.8 mmol BPO were added. The solution was heated cautiously to 75°C, and this temperature was held for 5 h. After cooling to room temperature, the deep red solution was slowly poured into 1200 ml methanol to precipitate the brown

polymer. After filtration and several washing intervals with hot methanol the polymer was dried at 50°C under vacuum to get the bromidepoly(ether sulfone)BPESF-c. Yield: 28.5 mmol (95.0%). The preparation processes were depicted in Scheme 1.The reaction conditions and properties of BPESFs were listed in Table 1.

Methyl imidazolium functionalization of the bromide poly(ether sulfone)s (MIPESFs)

To a solution of BPESF-c(1.2000 g) in dry DMAc, 1-methylimidazole (4 mL) in DMAc was added drop wise. The reaction mixture was heated to 75°C for 48 h under nitrogen. After this time, the reaction mixture was cooled to room temperature and precipitated into ethyl acetate (800 mL) followed by acetone (600 mL). The resulting polymer was collected by filtration and polymer was dried at 60°C under vacuum to give the methyl imidazolium-functionalized copolymer, that was MIPESF-c as a pale brown powder (1.0562 g). The preparation processes were depicted in Scheme 1.

The other MIPESFs were synthesized using the similar procedure as described for synthesis of MIPESF-c. The reaction conditions and properties of MIPESFs were listed in Table 2.

Membrane Preparation

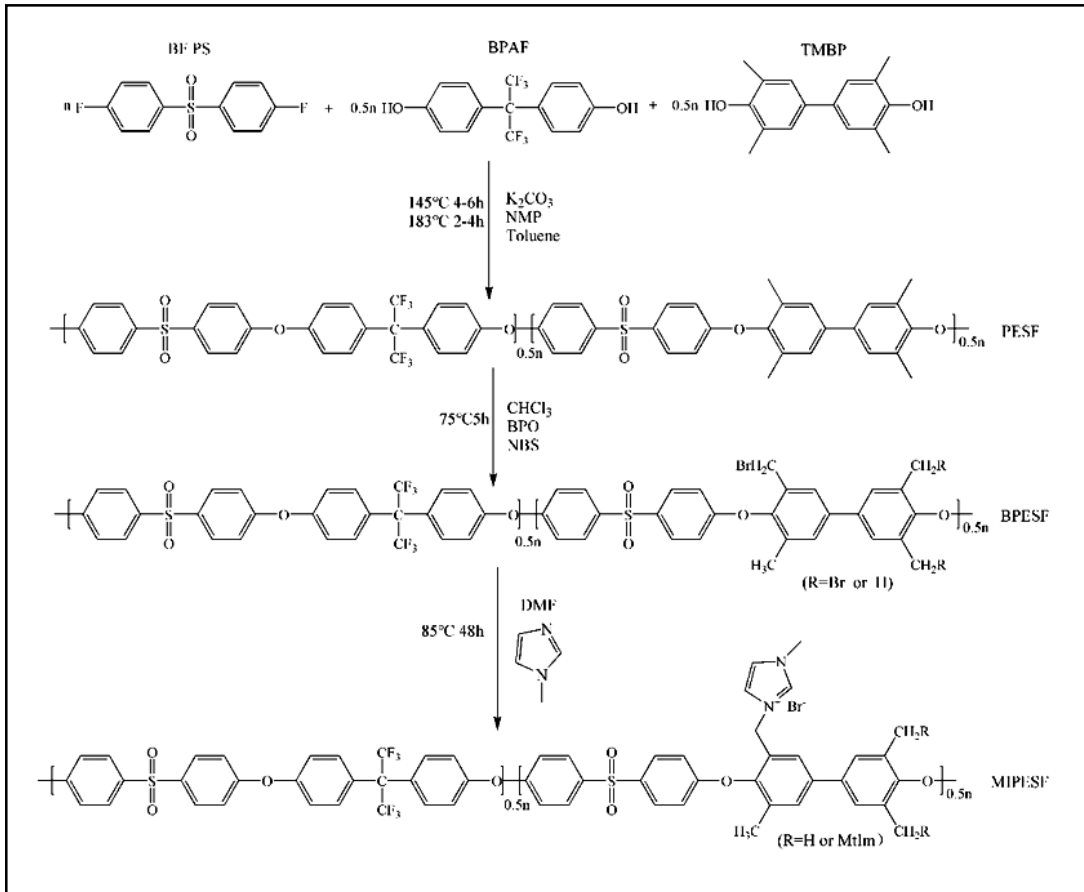
MIPESFs(0.2 g) was dissolved in DMAc (20 mL) to form a dilute solution. The solution was cast on a flat glass plate and dried in oven at 60°C for 24h to give a thin 30-50 μm thick, transparent and tough membrane.

Gas permeation test

The gas permeation properties of CO₂ and CH₄ for membranes were determined using a constant volume/variable pressure technique as described previously^[19]. A schematic diagram of the gas-permeation apparatus is exhibited in Fig. 1. Gas permeability under steady-state is determined by the following equation:^[19]

$$P = \frac{273}{76} \frac{Vl}{A\Delta p} \frac{dp}{dt} \quad (1)$$

Where P is the gas permeability in unit of Barrer (1 Barrer=10⁻¹⁰ cm³(STP) cm/(cm² s cmHg)=7.5×10⁻¹⁸m² s⁻¹ Pa⁻¹), V is the downstream volume (m³), A is the area of



Scheme 1. Synthesis of the MIPESF.

the membrane (m^2), T is the operating temperature (K), Δp is the transmembrane pressure difference (Pa), l is the membrane thickness (m) and dp/dt (Pa/s) is the rate of pressure increase at the permeate side in steady state.

The diffusion coefficient was obtained from the time-lag (θ) value according to the following equation:

$$D = L^2/6\theta \quad (2)$$

Where D is the diffusion coefficient ($10^8 \text{ cm}^2/\text{s}$), L is the membrane thickness (m), and θ is the time lag (s), which is given by the intercept of the asymptotic line of time - pressure curve to the time axis.

The S value was calculated by using equation

$$S = P/D \quad (3)$$

Where S is the (Solubility) coefficient ($10^3 \text{ cm}^3/\text{STP}/\text{cm}^3 \text{ cm Hg}$).

The ideal selectivity (α) of one penetrant (A) over another (θ) is given by

$$\alpha_{A/B} = \frac{P_A}{P_B} \quad (4)$$

TABLE 1. The reaction conditions and properties of polymers.

Sample	Monomer Feed (mmol)			Bromination Feed (mmol)			Bromination Temperature (°C)	Bromination Time (h)	Bromination ratio (%)	Yield %	[η] Inh ^c (dL/g)
	TMBP	BPAF	BFPS	K ₂ CO ₃	Repeated unit	BPO					
PESF	5	5	10	13	1	—	—	—	0	96	0.41
BPESF-a	—	—	—	—	1	0.04	0.5	75	42.4	95	0.38
BPESF-b	—	—	—	—	1	0.08	1	75	51.5	97	0.37
BPESF-c	—	—	—	—	1	0.16	2	75	58.1	95	0.43

^cTested in 0.5g dL⁻¹ solution in CHCl₃ at 25°C.

TABLE 2. The reaction conditions and properties of MIPESF.

Sample	Imidazolium functionalization Feed (mmol)		Imidazolium functionalization Temperature(°C)	Imidazolium functionalization time (h)	Yield (%)	[η] Inh ^c (dL/g)
	Repeated unit	1-methylimidazole				
MIPESF-a	1	25	75	48	86	0.379
MIPESF-b	1	25	75	48	84	0.366
MIPESF-c	1	25	75	48	85	0.382

c: MIPESF-a to c were tested in 0.5g dL⁻¹ solution in DMAc at 25°C.

Measurement

Nuclear magnetic resonance (NMR) spectra was recorded at 400MHz in a Bruker NMR instrument (model DRX) and listed in parts per million (ppm) downfield from tetramethylsilane(TMS). Thermal gravimetric

analysis (TGA) was carried out using a Perkin-Elmer, Pyris Diamond TGA analyzer under a nitrogen atmosphere (200 mL min^{-1}). The heating rate was $20^\circ\text{C min}^{-1}$ at temperatures ranging from 100°C to 600°C . The permeability experiments were performed using a VAC-V2 gas permeameter, which was supported by Labthink

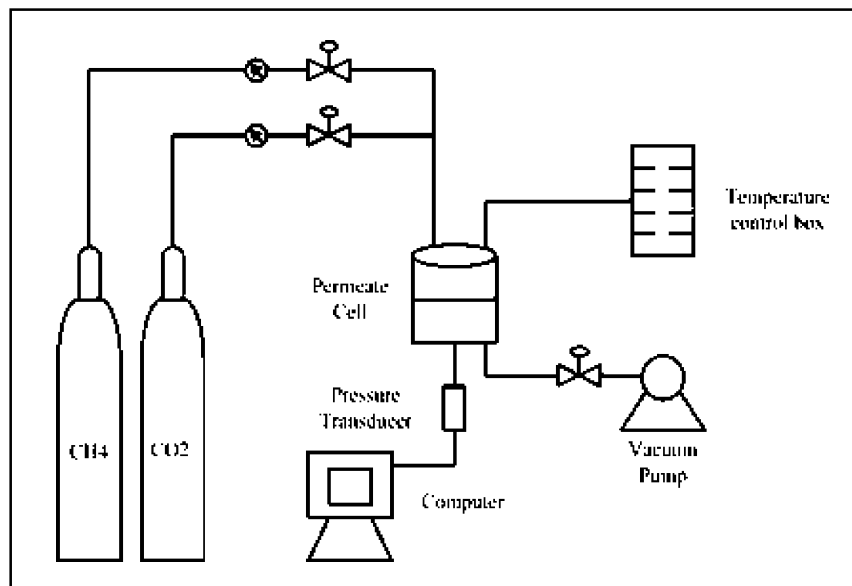


Fig. 1. Schematic diagram of the gas-permeation testing apparatus.

of the Ultimate Testing Technology. For each testing reported, at least three measurements were taken and the average value was calculated. For each testing reported, at least three measurements were taken and the average value was calculated. The error range was within $\pm 5\%$.

3. RESULTS AND DISCUSSION

Synthesis and characterization of PESFs and BPESFs

Poly(ether sulfone)(PESFs) was successfully synthesized by condensation copolymerization as shown in scheme 1. The polymerization of 2, 2-bis(4-hydroxyphenyl) hexafluoropropane (BPAF),3,3',5,5'-tetramethyl-4,4'-dihydroxybiphenyl

(TMBP) and bis(4-fluorophenyl)sulphone (BFPS) were carried out in anhydrous NMP solution in a nitrogen ambient. The reaction mixture was first controlled at 145°C for 3 h to azeotrope off water with toluene and then was heated to 185°C for a long time to afford a high-molecular-weight polymer. The polymer was confirmed by their $^1\text{H-NMR}$ spectrums accordingly. The $^1\text{H-NMR}$ spectrums of PESF is shown in Fig. 2, with proper assignment of all the resonance peaks. The peaks 2.0 ppm could be assigned to the chemical shifts of the methyl proton of the TMBP. All the other peaks were well assigned according to its chemical structure.

As illustrated in Scheme 1, the successful bromination of PESF was performed with NBS. To determine the bromination degree of the BPESFs, ¹H-NMR spectra was measured and presented in Fig. 3. The spectra indicate that

only the side chains of the PESF were brominated. When the aromatic backbone of the polymer is brominated, there must be signals around 6 ppm. By integration of the well separated signals from the methyl peak and the

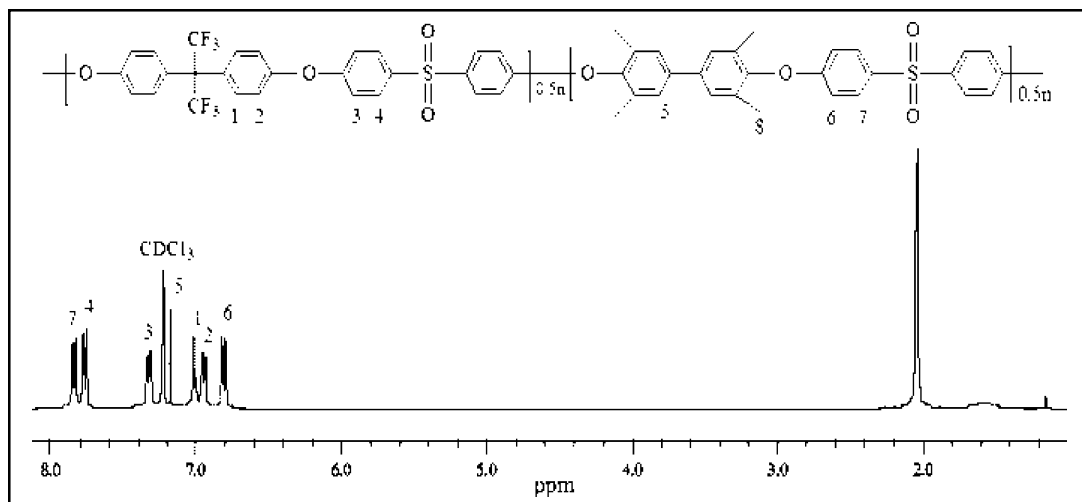


Fig. 2. ¹H-NMR spectrum of PESF in CDCl₃.

methylene peak the bromination degree was calculated according to the following equation, experimental bromination degree of BPESF-a-c is 42.4%, 51.5%, 58.1%, respectively.

$$X_{\text{CH}_2\text{Br}}(\%) = \frac{3 \times I_{\text{CH}_2}}{3 \times I_{\text{CH}_2} + 2 \times I_{\text{CH}_3}} \times 100\% \quad (5)$$

X_{CH₂Br}: bromination degree; I: Intensity of NMR signals.

Synthesis and characterization of MIPESFs

Further functionalization to the imidazolium-incorporated MIPAEK was carried out by treating a DMAc solution of BPESF with methyl imidazole. As shown in Fig.4, the ¹H NMR spectrum of MIPESF-c displayed the

characteristic peak of the imidazolium proton (H_i) at 9.2 ppm and methyl protons (H_j) of methyl imidazole at around 1.9 ppm, indicating successful incorporation of the imidazolium group.

Thermal stability of the MIPESFs membranes

Thermal stability of the MIPESFs membranes were investigated by TGA (Fig.5). All the membranes subsequently displayed three-stage weight loss behavior. As for the MIPESFs membranes, the first stage was from 100 to 200 °C, likely due to the loss of imidazolium groups. The second and third-stages of the MIPESFs membranes from 240 to 400°C and ~500°C were due to the decomposition of the

polymer side chains and main chains, respectively. This study revealed that these types of membranes were stable up to 100°C without losing their functional properties.

Effect of imidazolium groups on gas permeability

Permeation measurements were carried out using pure CO₂ and CH₄ at different pressures

and temperatures. To investigate the effect of imidazolium groups on gas permeability, a series of imidazolium-functionalized poly(ether sulfone)s were fabricated. The permeability of membranes with different imidazolium contents is shown in Fig. 6 and Fig. 9, respectively. Fig. 8 (a) and Fig. 11 (a) show the solubility of CO₂ at different pressures and temperatures. We can see that the solubility of CO₂ of the

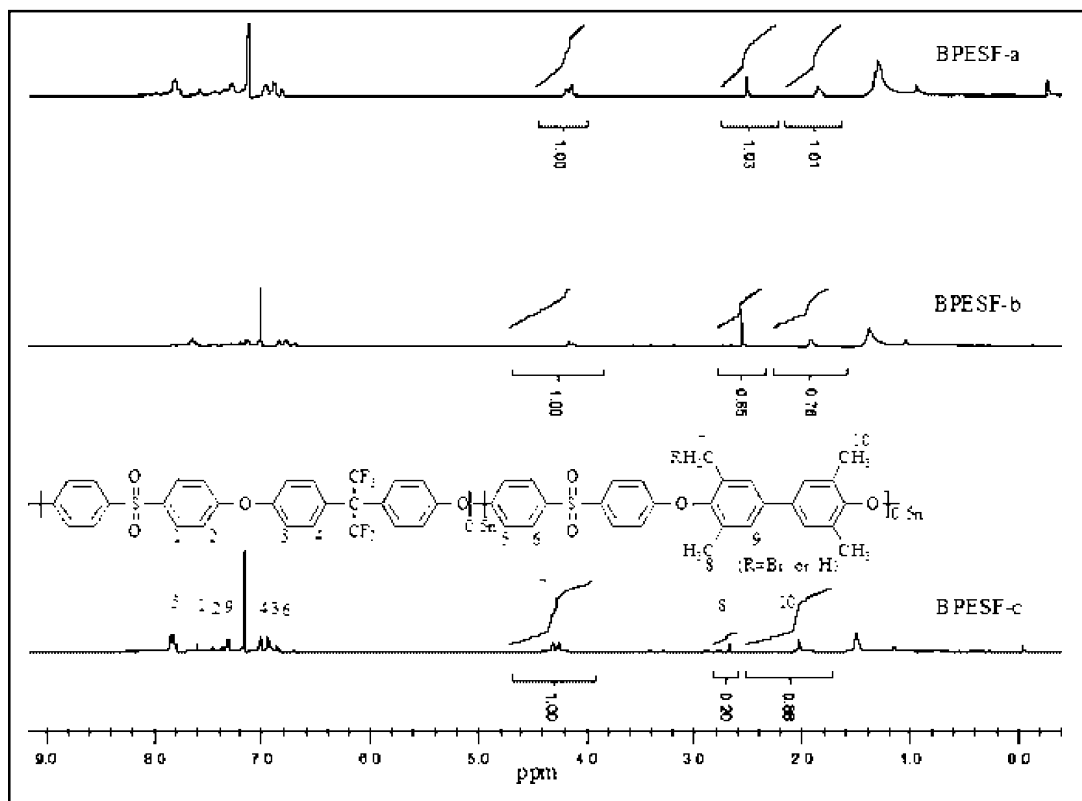


Fig. 3. ¹H-NMR spectrum of BPESF in CDCl₃.

membrane increased with increasing the imidazolium groups at different pressure and temperature. However, the solubility coefficient (S) of CH₄ was decreased (Fig. 8 (b) and Fig. 11

(a)). This can be explained by the fact that the correlation between the unshared pairs of electrons of N atoms in imidazolium groups and the negatively charged oxygen atoms of CO₂

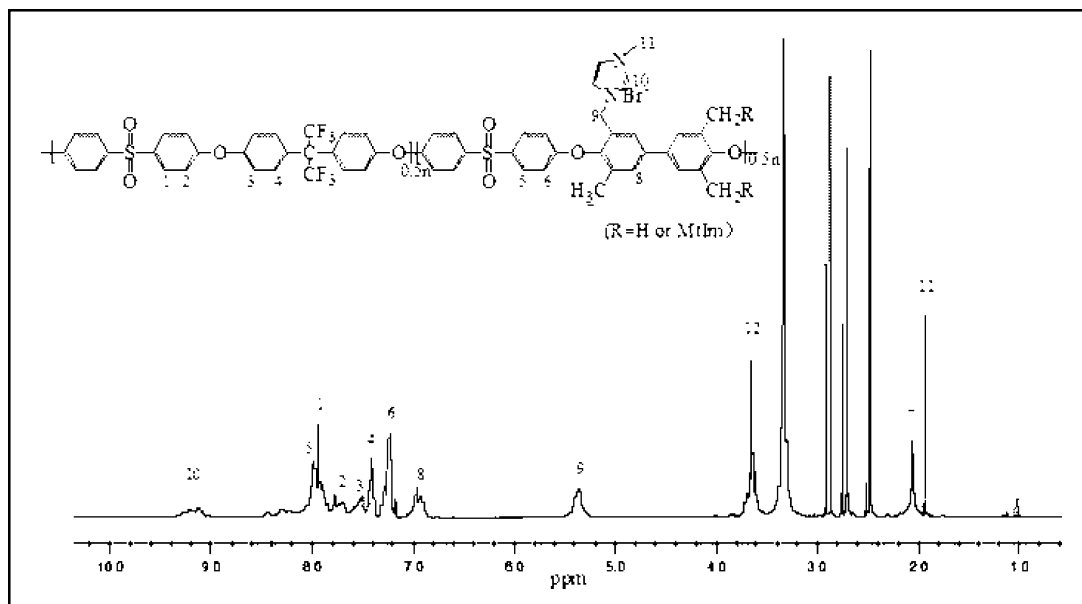


Fig. 4. ¹H-NMR spectrum of MIPESF in DMSO-*d*₆.

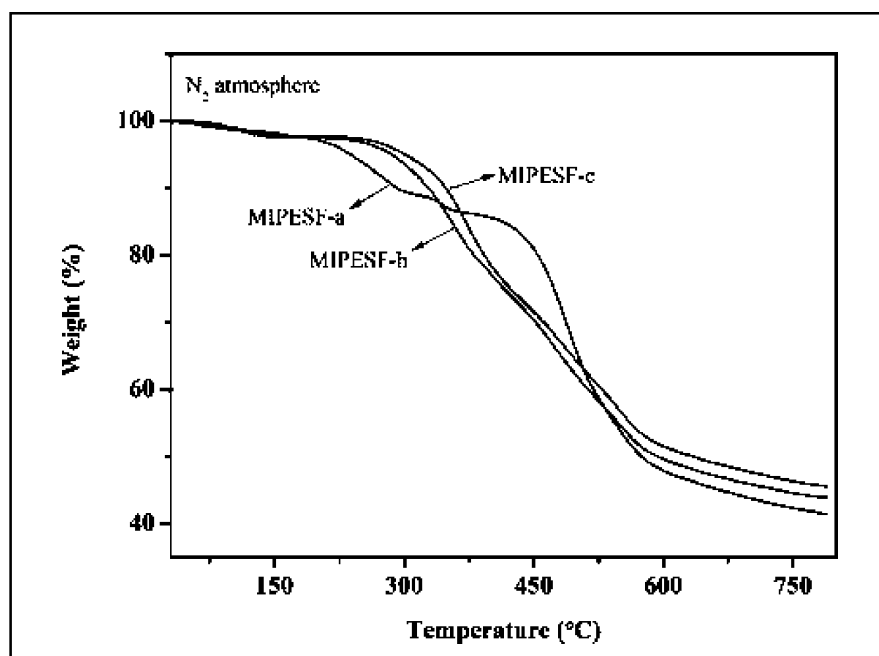


Fig. 5. The TGA curves of MIPESF-a, MIPESF-b and MIPESF-c.

increases CO₂ solubility in MIPESFs membranes. It was suggested that the imidazolium group could facilitate or enhance CO₂ solubility. Gas permeability coefficient is decided by two factors, diffusion and solubility coefficient; so the solubility enhancement can improve the gas permeability. For example, MIPESF-c membrane exhibits the solubility coefficient of $34.91 \times 10^3 \text{ cm}^3/\text{STP}/\text{cm}^3 \text{ cm Hg}$, which is higher than the solubility coefficient of MIPESF-a membrane ($24.64 \times 10^3 \text{ cm}^3/\text{STP}/\text{cm}^3 \text{ cm Hg}$) at 25°C and 1.0 atm.

Effect of pressure on gas permeability at 25°C

Pressure effects on membrane performance were studied over a pressure range of 0.5-1.5 atm (single gas at 25°C). Fig.6 show the permeability of CO₂ and CH₄ for membranes as a function of the pressure. From above program, the permeability of CO₂ and CH₄ decreases with increasing pressure. For instance, the CO₂ permeability of MIPESF-c membrane declined by around 15.6% at 1.5 atm which compared with 0.5 atm. While the CH₄ permeability

declined by around 34.0% at 1.5atm to 0.5atm. In polymers, the result of that was reported: At higher pressure, the contribution of the Langmuir region to the overall permeability diminishes and gas permeability approaches a constant value associated with simple dissolution (Henry's law) transport^[20]. In this examine, the diffusion coefficients of different pressures are shown in Fig.7. For MIPESF-c, diffusion coefficient increased by around 11.1% and 9.4% for CO₂ and CH₄ at 1.5 atm which compared with 0.5 atm, respectively. The others groups were the same rule of changing.

Effect of temperature on gas permeability at 1atm

The measurements were carried out with CO₂ and CH₄ at different temperature of 25°C-55°C and 1.0 atm (Fig.9). As shown in Fig.9, the permeability of CO₂ and CH₄ increases with increasing temperature. For all membranes, the performance of the gases showed a typical activated diffusion behavior and at higher temperatures(Fig.10). For example, the CO₂ permeability of MIPESF-c membrane declined

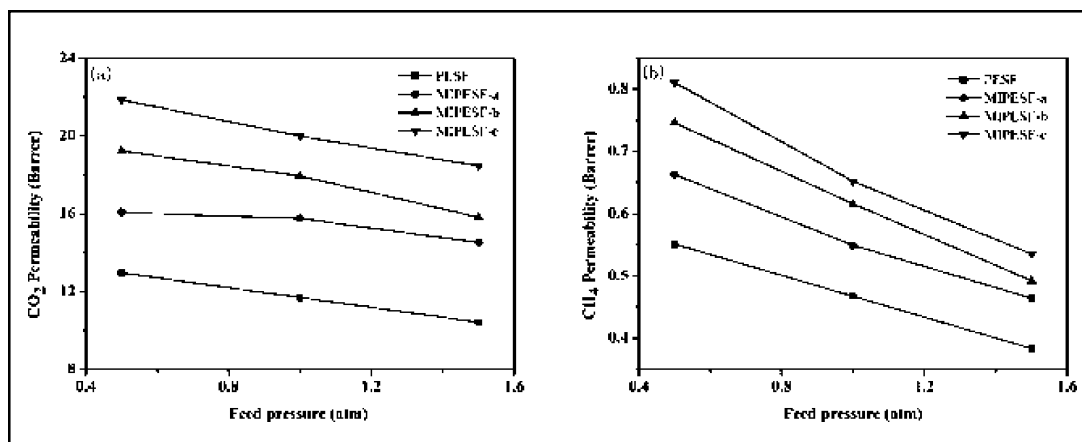


Fig. 6. Permeability of CO₂(a) and CH₄ (b) at 25° and different pressures.

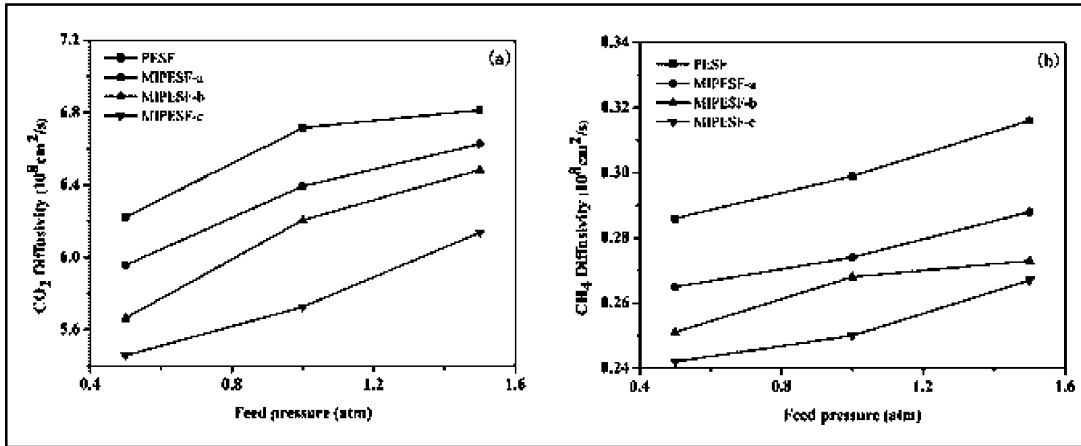


Fig. 7. Diffusivity of CO₂ (a) and CH₄ (b) at 25° and different pressures.

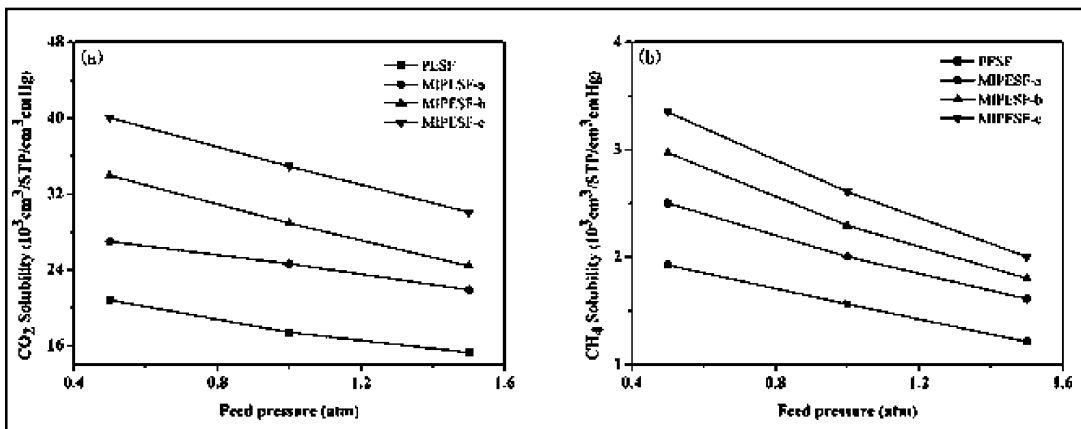


Fig. 8. Solubility of CO₂ (a) and CH₄ (b) at 25° and different pressures.

by around 16.6% at 25°C which compared with 55°C at 1.0 atm. While the CH₄ permeability declined by around 24.1% from 25°C to 55°C. This enhancement in permeability with temperature was due to an increase in diffusivity of the gas as well as an enhancement in flexibility of the polymer chains [21].

Membrane selectivities for CO₂/CH₄ gas pairs

As shown in Fig.12, the membranes show the higher selectivity for CO₂/CH₄ gas pair. CO₂/CH₄ selectivity increases monotonously with increasing pressure as shown in Fig.12 (a).

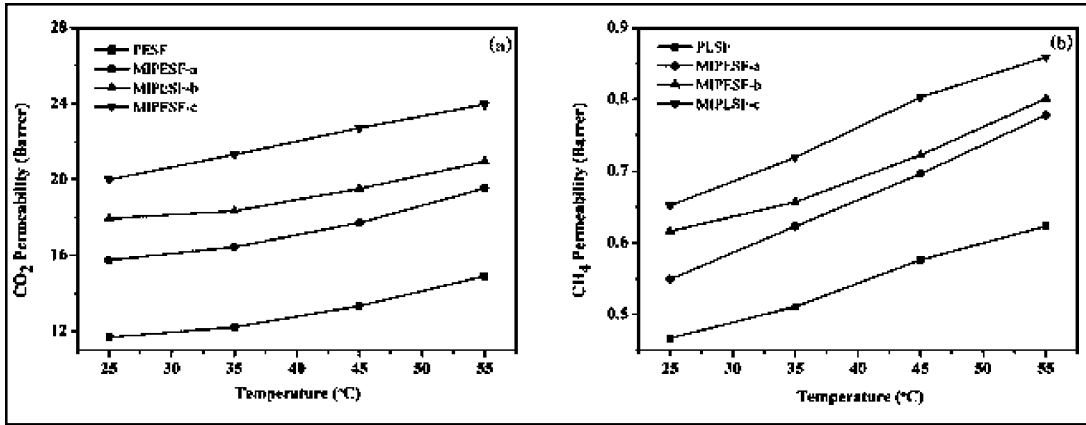


Fig. 9. Permeability of CO₂(a) and CH₄ (b) at 1.0 atm and different temperatures.

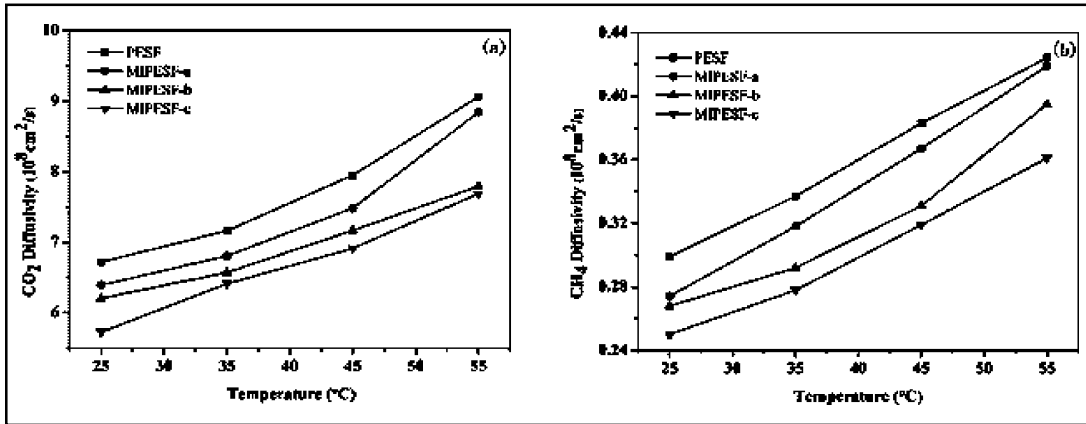


Fig. 10. Diffusivity of CO₂ (a) and CH₄ (b) at 1.0 atm and different temperatures.

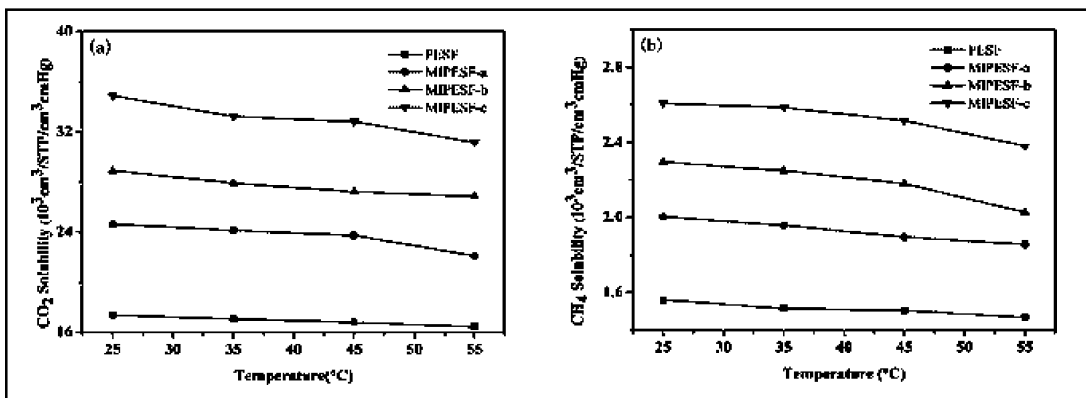


Fig. 11. Solubility of CO₂ (a) and CH₄ (b) at 1.0 atm and different temperatures.

It is due to more increment of CO₂ permeation because of the following two reasons: (1) imidazolium as facilitated transport segment for CO₂ (2) lower kinetic diameter of CO₂ which causes easier diffusion. The Fig.12 (b) shows the effect of temperature on CO₂/CH₄ ideal

selectivity at 1.0atm. As shown in Fig.12(b), CO₂ selectivity over CH₄ decreases with rising temperature. This is because of more increment in permeation of CH₄ in comparison with CO₂.

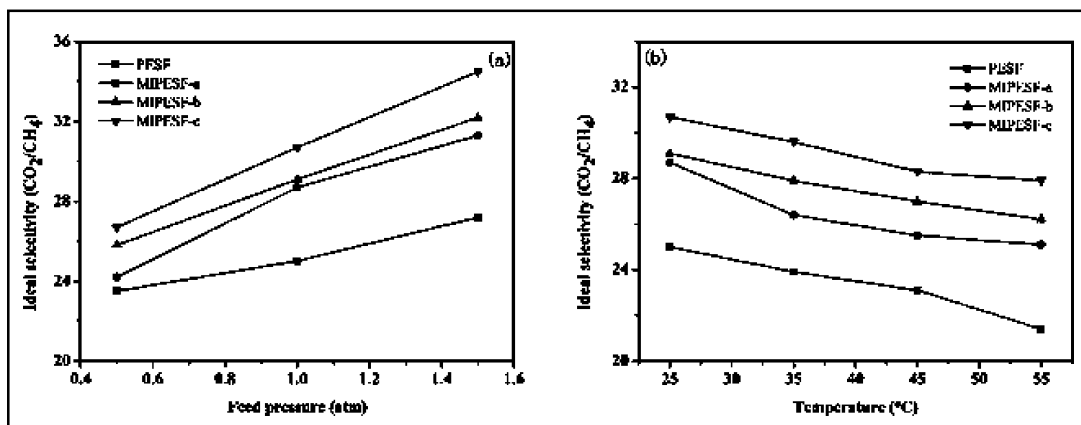


Fig. 12. Ideal selectivity of CO₂/CH₄ at different pressures (a) and at different temperatures (b).

4. CONCLUSIONS

In summary, the copolymers comprising different imidazoliumionic groups were synthesized and characterized for gas separation membranes. The synthesized membranes excellent performance and better CO₂/CH₄ ideal selectivity. Especially the membrane derived from MIPESF-c possessed better performances in terms of permeability (18.5 Barrer) and CO₂/CH₄ ideal selectivity (34.5). In conclusion, the membranes are suitable for as a gas separation membrane for CO₂ separation.

ACKNOWLEDGEMENTS

The authors would like to thank for the Natural Science Foundation of China (51572185) financial support of this work.

REFERENCES

1. M. H. Abdul, H. Mukhtar, S. M. Shima, O. M. Roslee and T. Murugesan, *J. Appl. Polym. Sci.* 133(2016) 42946.
2. N. Alaslai, B. Ghanem, F. Alghunaimi, E. Litwiller and I. Pinnau, *J. Membr. Sci.* 505(2016) 100.
3. A. Car, C. Stropnik, W. Yave and K. V. Peinemann, *J. Membr. Sci.* 307(2008) 88.
4. J. Cheng, L. Hu, Y. Li, C. Ji, J. Zhou and K. Cen, *RSC Adv.* 6(2016) 2055.
5. Q. Fu, J. Kim, P. A. Gurr, J. M. P. Scofield, S. E. Kentish and G. G. Qiao, *Energy Environ. Sci.* 9(2016) 434.
6. Y. Zhang, J. Sunarso, S. Liu and R. Wang, *Int. J. Greenh. Gas Control.* 12(2013) 84.
7. Y. C. Xiao, B. T. Low, S. S. Hosseini, T. S. Chung and D. R. Paul, *Prog. Polym. Sci.* 34(2009)561.

8. A. Mondal and B. Mandal, *J. Membr. Sci.* 460 (2014) 126.
9. X. Wang, H. Chen, L. Zhang, R. Yu and L. J. Yang, *J. Membr. Sci.* 470(2014) 237.
10. S. Ghosh and S. Banerjee, *J. Membr. Sci.* 497(2016) 172.
11. C. Zhang, Y. Wu, Y. Zhang, Y. Bai, J. Gu and Y. Sun, *J. Membr. Sci.* 508(2016) 136.
12. J. H. Lee, J. P. Jung, E. Jang, K. B. Lee, Y. S. Kang and J. H. Kim, *J. Membr. Sci.* 502(2016) 191.
13. M. Z. Pedram, M. Omidkhah, A. E. Amooghin and R. Yegani, *Polym. Eng. Sci.* 54(2014) 1268.
14. W. S. Chia, S. U. Hong, B. Jung, S. W. Kang, Y. S. Kang and J. H. Kim, *J. Membr. Sci.* 443(2013) 54.
15. Y. W. Yu, B. J. Liu, Y. Wang, S. Y. Liu, X. B. Li, Z. Liu and Z. H. Jiang, *High Perform. Polym.* 26(2014) 401.
16. Y. Y. Gu and T. P. Lodge, *Macromolecules* 44(2011) 1732.
17. I. Kammakam, S. Nam, and T. H. Kim, *RSC Adv.* 6(2016) 31083.
18. T. C. Merkel, V. I. Bonder, and I. Pinnau, *J. Polym. Sci. Part B: Polym. Phys.* 38(2000) 415.
19. D. Zhao, J. Ren, H. Li, X. Li and M. Deng, *J. Membr. Sci.* 467(2014) 41.
20. M. M. Khan, V. Filiz, G. Bengtson, S. Shishatskiy, M. M. Rahman, J. Lillepaerg and V. Abetz, *J. Membr. Sci.* 436(2013) 109.
21. S. Sorribas, B. Zornoza, C. Téllez and J. Coronas, *J. Membr. Sci.* 452(2014) 184.

Received: 14-06-2017

Accepted: 14-09-2017