The Researches on Polymers of Intrinsic Microporosity Membranes for Separation

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Abstract. Polymers of intrinsic microporosity (PIMs) are novel class of porous materials with well-defined microcavities and high free volume elements. As the typical soluble PIMs, PIM-1 has received much attention in the field of gas separation, pervaporation and organic solvent nanofiltration, due to its microporosity, easy processability, high surface area and superior hydrophobicity. The PIM membrane with unique rigid and contorted macromolecular backbone structure showed excellent performance in gas and liquid separation, especially high CO_2 permeance and excellent CO_2/N_2 and CO_2/CH_4 separation factors. In general, the PIM membranes with unique characteristics will be the most promising candidates for industrial separation.

1. Introduction

Traditional separation technologies such as condensation and distillation have always been regarded as energy-intensive processes in almost all manufacturing industries. Compared with the above traditional separation technologies, membrane separation with no phase transition has the following advantages [1, 2]. Firstly, membrane separation can obtain high separation efficiency with low energy consumption [3, 4]. Secondly, the relatively simple operation process is beneficial for the expansion of production and automation [5]. All of these factors will contribute to the successful application of the membrane separation in various industrial fields.
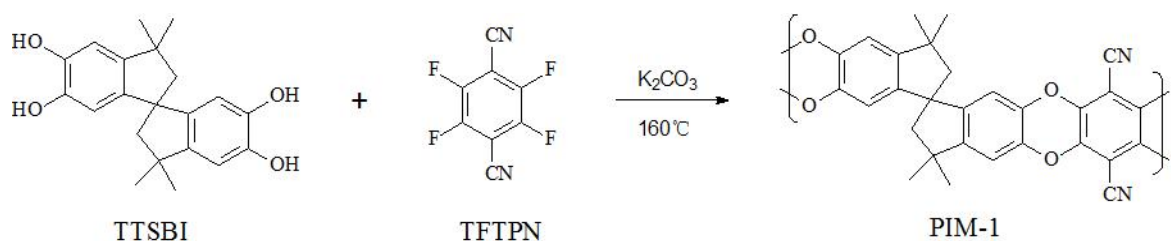

Figure 1. Reaction scheme for PIM-1

The selection of a suitable membrane material has a crucial influence on the membrane separation performance. The rapid development of porous materials effectively promotes the progress of membrane materials. Conventional inorganic porous materials such as zeolites, ceramics, TiO_2 and so on have been successfully used as membrane materials and the good separation performance have been achieved [6-8]. However, the inorganic membrane materials with high rigidity and expensive cost have the difficulty in production, restricting its further development [9]. As a new kind of organic-inorganic composite materials, metal-organic frameworks(MOFs) with high porosity and surface area have successfully been applied in membrane separation process. Recently, MOF materials have been prepared as MOF membrane by the in-situ growth, seed growth and chemical modification method. These MOF membranes have shown excellent separation performances. However, the weak mechanical stability restricts the application of MOF membrane in the practical industry [10-13].

As a microporous organic polymer, PIM-1 with well-defined microcavities and high free volume was first prepared by McKeown et al [14]. It has received a large amount of attention in the field of gas separation, pervaporation and organic solvent nanofiltration. As the typical soluble PIMs, PIM-1 with uniform pore size, high specific surface area, excellent physical and chemical stability is prepared by the polycondensation reaction of tetrafluoro-monomer (TFTPN) and tetrahydroxyl-monomer (TTSBI) (Figure 1). The micropores of PIM-1 are derived from its special rigid ladder-like and contorted backbone structure. Compared with the inorganic porous materials, PIM-1 possesses excellent processability and can be readily dissolved in tetrahydrofuran (THF), dichloromethane (CH_2Cl_2), and chloroform ($CHCl_3$), which will be greatly useful for the preparation of PIM-1 membrane. Furthermore, the PIM-1 with the nitrile group in the molecular chain is easily to be functionalized at the molecular level to improve the membrane performance.
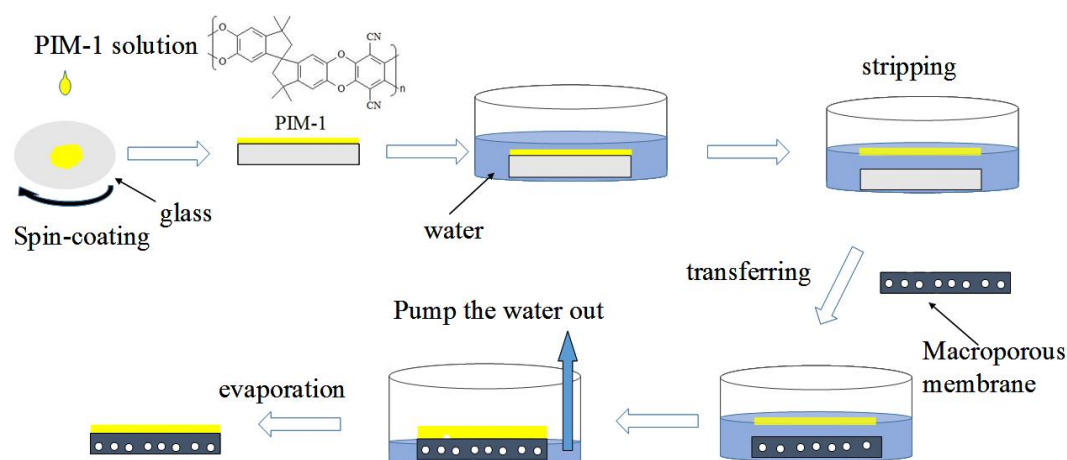

Figure 2. Schematic of the preparation of PIM-1 TFC membrane by the spin-coating method

2. The Preparation of PIM Membranes

The methods for preparation of PIM membranes mainly include solvent evaporation, spin coating and interfacial polymerization. Budd et al. first successfully prepared the free-standing PIM-1 membrane by solvent evaporation method in 2003 [15]. After that, the conditions of solvent evaporation were optimized by some more researchers. Moreover, the researchers also reduce the thickness of the membrane to the nanometer degree to improve membrane performance. The fabrication of thin film composite (TFC) membranes is a feasible method. In recent years, PIMs have obtained a great deal of attention in the preparation of TFC membranes. Fritish et al. produced PIM-1/PAN TFC membranes by dip-coating PIM-1 solution onto the PAN support with no signs of compaction and aging of PIM-1 layer [16]. As shown in Figure 2, Livingston et al. reported the spin-coating method for the fabrication of ultrathin PIM membrane with the exceptionally fast permeation of n-heptane [17].
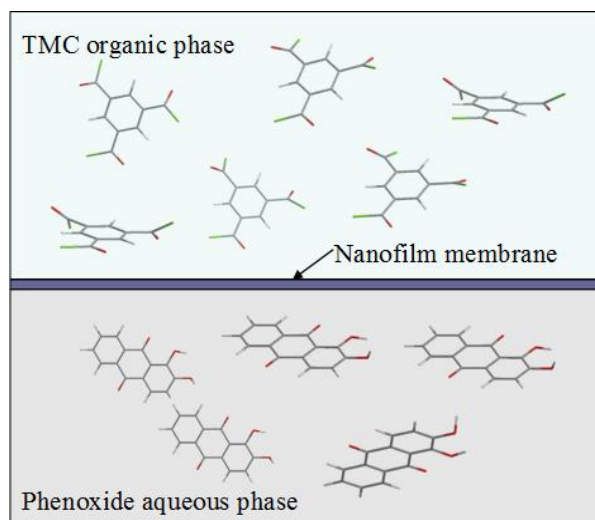
Figure 3. Schematic of the preparation of PIM-1 TFC membrane by the interfacial polymerization method

Interfacial polymerization is also an effective method to fabricate PIM TFC membrane. As shown in Figure 3, Livingston et al. successfully prepared the ultrathin polyarylate nanofilms with enhanced microporosity by the method of interfacial polymerization. The prepared membrane with the thickness down to 20 nm displayed outstanding separation performance in organic solvent. Compared with the coating method, the interfacial polymerization method is relatively complex [18].

3. PIM Membranes Used for Separation

3.1. Gas separation

The mechanism of gas permeation through the polymer membranes is the solution-diffusion model. Solubility coefficient is correlated to the affinity between polymer and gas molecules while the diffusion coefficient is related to the size of gas molecules and free volume of polymer [19]. Generally, the polymer membrane always faces the trade-off phenomenon, since the high permeability always couples with the low selectivity. The rigid structure and high free volume of PIMs provide the chance to break through the trade-off effect. Cornelius et al. reported that PIM-1 and PIM-7 showed the high permeability with the extraordinary selectivity for O_2/N_2, beyond the Roberson curve [20]. Budd et al. reported that PIM-1 showed a high CO_2 permeability and kept an excellent selectivity of CO_2/N_2 and CO_2/CH_4 which all surpassed the Roberson curve, due to the affinity between PIM-1 and CO_2 [21].

Table 1. Gas permeability and selectivity of some PIM membrane

Polymer	Permeability (Barrers)					Selectivity				Ref.
	H_2	CO_2	O_2	N_2	CH_4	O_2/N_2	CO_2/N_2	H_2/CO_2	CO_2/CH_4	
PIM-1	5010	13600	2270	823	1360	2.8	16.5	0.37	10	20
amine-PIM-1	876	295	216	55.7	82.8	3.9	5.3	2.97	3.56	22
Thioamide-PIM	92	150	19	3.9	8.7	4.87	38.46	0.61	17.24	24
Carboxylated PIM-1	408	620	110	24		4.58	25.83	0.66		23
PIM-Photo oxidative	2000	2100	600	100	34	6	21	0.95	61.76	25
PIM-Thermal oxidative	900	1100	270	13	15.7	20.77	84.62	0.82	70.06	26

The functionalization of PIM membrane can further be used to improve the gas separation performance. Guiver et al. studied the gas separation performance of the carboxylated PIM-1 membrane. They chose sodium hydroxide solution to hydrolyze the PIM-1 membrane and controlled the hydrolysis degree by changing the reaction temperature and time [23]. In 2011, Budd et al. successfully prepared the thioamide-PIM-1 membrane, which was fabricated by the aminylation of PIM-1 membrane using the mixture of P_2S_5 and Na_2SO_3 as the amination reagent. Compared with PIM-1 membrane, the aminylated-PIM-1 membrane had higher CO_2/N_2 selectivity of 38.5 [24]. As shown in Table 1, there are some other ways to improve the separation performance of PIM membrane, such as thermal oxidation crosslinking, photo-oxidative and so on [25-26].

3.2. Pervaporation
Pervaporation has been widely used to separate the mixture of organic substances and water. Generally, PIMs exhibit strong solvent resistance, which could only be dissolved in chloroform, tetrahydrofuran, dichloromethane and show excellent solvent stability in alcohol solution. Therefore, PIM membranes are suitable for the pervaporation of alcohol/water mixtures. Zhang et al. prepared the PIM-1 membrane and used it in the pervaporation of ethyl acetate solution with the high flux of 39.5 kg μm m^{-2} h^{-1} and selectivity of 189 [27].
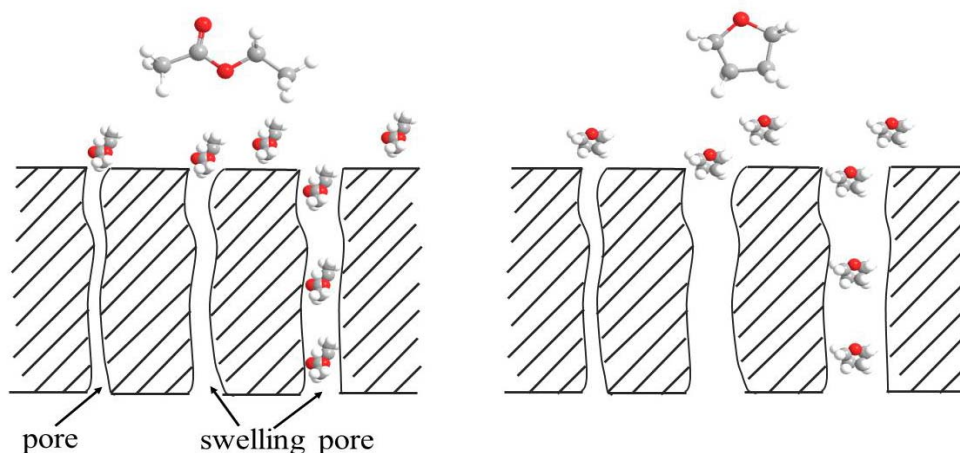

Figure 4. Different swelling degree of PIM-1membrane's pores to different solvents

3.3. Organic solvent nanofiltration (OSN)
The PIM-1 membrane with excellent hydrophobicity and high porosity can also be used in the organic solvent nanofiltration. Volkov et al. fabricated the free-standing PIM-1 OSN membrane whose thickness was 20 μm. The swelling and the affinity to organic substance of the PIM-1 membrane were observed to improve the membrane flux [28]. Other researchers tended to improve the membrane flux by decreasing the thickness of PIM-1membrane. Livingston et al. successfully prepared the ultrathin PIM-1 films (35-660 nm) and applied them into the separation of hexaphenylbenzene/ heptane solution. The reduction of the membrane thickness significantly increased the flux and all membranes guaranteed the 90% rejection of hexaphenylbenzene (HPB) from heptane solution [17].

4. Conclusions and outlook
In brief, PIM membranes with well-defined microcavities, high free volume, easy processability and excellent mechanical stability have attracted a great deal of attention in gas and liquid separation, pervaporation and organic solvent nanofiltration. The prepared PIM membranes with unique rigid and contorted macromolecular backbone structure have shown excellent separation performance. Future developments of PIM membranes will focus on the design of new methods to reduce cost and the improvement of the long-term stability for industrial application.

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