MODIFICATION PROGRESS OF POLYMER MEMBRANES FOR GAS SEPARATION

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Abstract. The research on polymer membranes for gas separation has surprisingly blossomed during recent decades. Many modification techniques have been developed to improve the separation properties of polymermembranes. In this review, we give a systematic summary of the main aspect of polymeric gas separation membranes related to their physical and chemical modification, and propose perspectives for the future developments.

1. INTRODUCTION

The field of gas separation membranes is a dynamic and rapidly growing field [1,2]. Currently the worldwide membrane market has a steady growth of ~15% each year [3]. The development of membrane processes for gas mixture separation has exhibited a remarkable progress in the last two decades. Gas separation membranes as an important membrane unit employed widely throughout the chemical industries have attracted much attention for its advantages of energy saving, low capital cost, and no pollution [4-8].

Gas separation membranes have found many applications including O_2/N_2 separation, CO_2/N_2 separation, vapor–vapor separation, dehydration of air and the removal of volatile organic compounds from effluent streams [9]. The membranes used for gas separation can be roughly categorized into three kinds: porous inorganic membranes, dense polymeric membranes, and organic–inorganic hybrid membranes [10-12].

Polymeric membranes can be used for separation of nearly all imaginable gas mixtures, such as natural gas treatment, hydrogen isolation and re-

covery, oxygen and nitrogen enrichment from air [4,13]. Many efforts were made in order to improve gas separation performance including permeability and selectivity of polymeric membrane. Despite these efforts, an important constraint in the development of these membranes for gas separation applications are the permeability and selectivity indicated in conflict with the trade–off curve, demonstrated by Robeson (Fig. 1) [14-17]. Pure organic polymeric membranes can reach but seldom surpass the limit of the permeability–selectivity trade–off the Robeson upper bound [12,18]. The selectivity, thermal stability and chemical stability have challenges for almost all polymeric membranes [19,20]. Not only do the membranes have relatively poor separation performance, but they exhibit severe swelling. Hence, in addition to the development of novel membrane materials, the modifications of existing polymeric membrane materials have become an important part of the study of gas separation membranes [21].

Many modification methods were explored to enhance the separation performance and physical properties of polymeric membranes. This review thoroughly investigates the effective modification meth-

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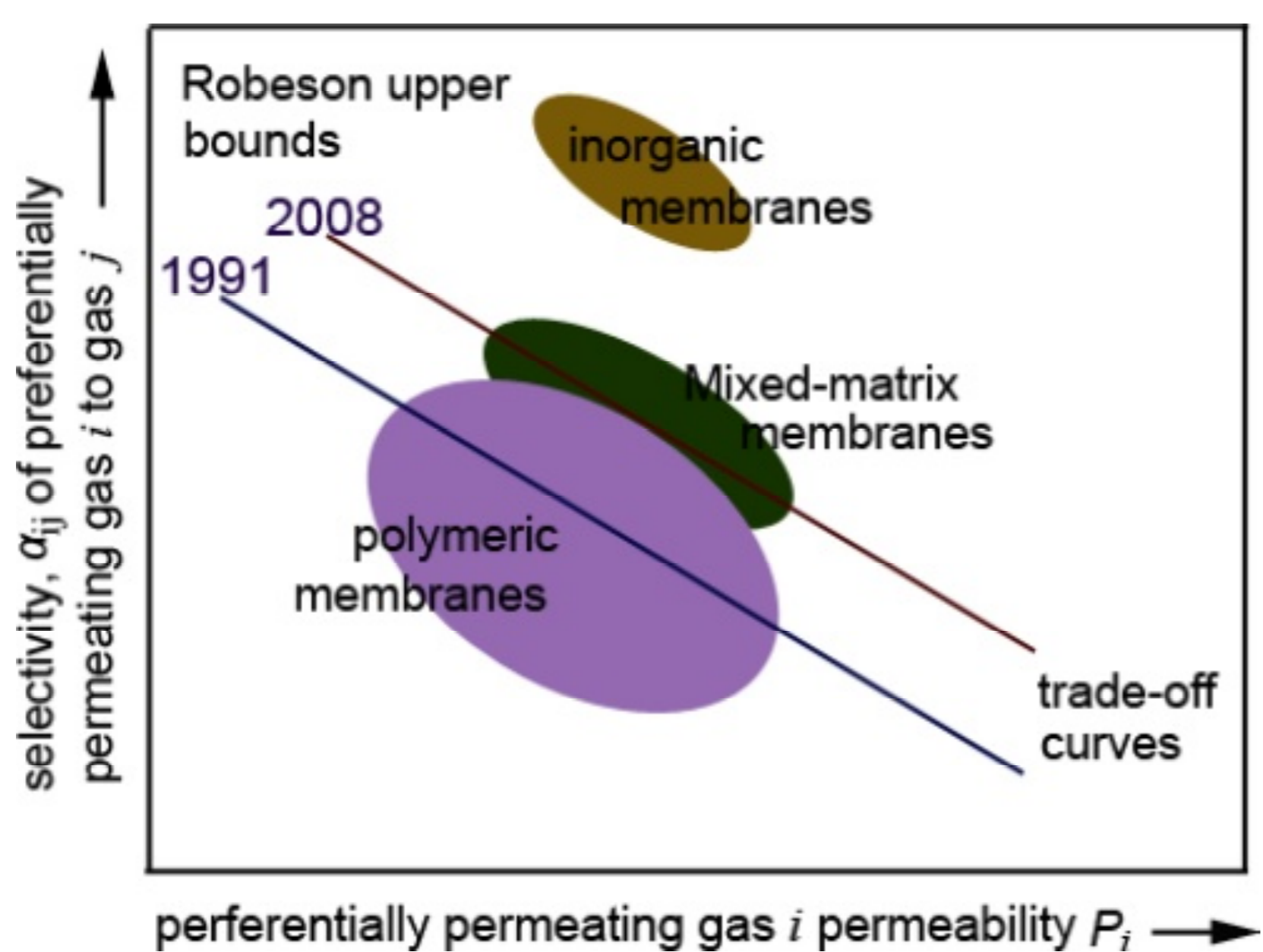Corresponding author: B. Yu and H. Cong, e-mail: yubingqdu@yahoo.com

Fig. 1. Schematic presentation of the trade–off between permeability and selectivity with the 1991 and 2008 Robeson upper bounds, reprinted with permission from H. B. T. Jeazet, C. Staudt and C. Janiak // Dalton T. **41** (2012) 14003, (c) 2012 The Royal Society of Chemistry.

ods that can be exploited to improve the polymeric membranes' permeability and selectivity. Besides, a brief outlook for the potential usage of these modified membrane materials was also given.

2. PHYSICAL MODIFICATION

By modification of the existing polymers, many gas separation membranes' performance can be improved. According to the way of modification, it can be categorized as physical modification and chemical modification. Generally, physical modification is realized by blending or coating to prepare composite membrane, which is very simple compared with other methods. This modification method is based on the complementary principle.

2.1. Blending modification

The blending modification is the common method of physical modification with its advantages of simple and easy operation, which can used to improve the structure of the materials and the property of the membranes [22-25]. After the blending modification, the membrane material could not only avoid the disadvantage of the single component, but also can possess completely special property compared with the single component membrane. In this method, the polymer is blended with two or more kind of polymers or inorganic/metal nanoparticles in the same solvent. During the blending process, the polymer molecules penetrate, diffuse and combine each other via polar and non–polar force. The homogene-

ity of the resultant composite relied on external forces such as stirring [26].

Many materials including inorganic and organic materials could be incorporated into polymers to enrich their property. Inorganic materials that could be blended with polymers include silica (SiO_2) [27,28], titanium dioxide (TiO_2) [29], zirconium dioxide (ZrO_2) [30], alumina (Al_2O_3) [31], zinc oxide (ZnO) [32] and some small molecule inorganic salts. Besides, carbon nanomaterials also could be used to blend with polymers to improve their selectivity for gas separation [33-35].

Many researchers had studied the blending modification on the polymeric membrane materials. For example, Park *et al.* [36] found that by adding a variety of materials with the property of separation, the gas separation performance of the polymeric membrane could be improved. Specifically, the addition of poly(dimethylsiloxane) (PDMS) into polyester membrane materials had a positive effect on the permeability and selectivity. Seung *et al.* [37] investigated the homogeneous gas permeability of polystyrene (PS)/poly(2,6–dimethyl–1,4–phenylene oxide) (PPO) blending system. They found that the compatibility of PS/PPO was good, and the freedom volume of the slowly cooled PS/PPO membranes was less than that of the quenched membranes. Hashemifard *et al.* [38] prepared polyetherimide (PEI)/polysulfone (PSF) composite membrane by the co–casting technique. Chung and Xu investigated the polybenzimidazole and polyetherimide composite hollow fiber membranes. Thermal mechanical analyzer data indicated that these composite hollow fibers were miscible blend membranes [39].

In recent years, metal–organic framework materials (MOFs) area novel class of microporous materials comprised of transition metals and transition metal oxides connected by organic linkages to create one–, two–, and three–dimensional microporous structures. They have high framework stability and highly selectivity for gas adsorption [40]. Blending polymer membranes with MOFs materials can result in improvement in permeability as well in selectivity for some gases compared to pure polymeric membranes [41]. Thin continuous MOF membranes for gas separation, such as MOF–5 [42], HKUST–1 ($Cu_3(BTC)_2$) [43], Cu–(hfipbb) ($H_2hfipbb)_{0.5}$ [44], $Zn_2(cam)_2$dabco (Zn–CD) [45], ZIF–8 and ZIF–9 [46,47], have been reported. For instance, Adams *et al.* [48] filled a kind of MOFs (CuTPA) into polyvinyl acetate (PVAc) membrane and investigated the influence of CuTPA filling on the gas transport prop-
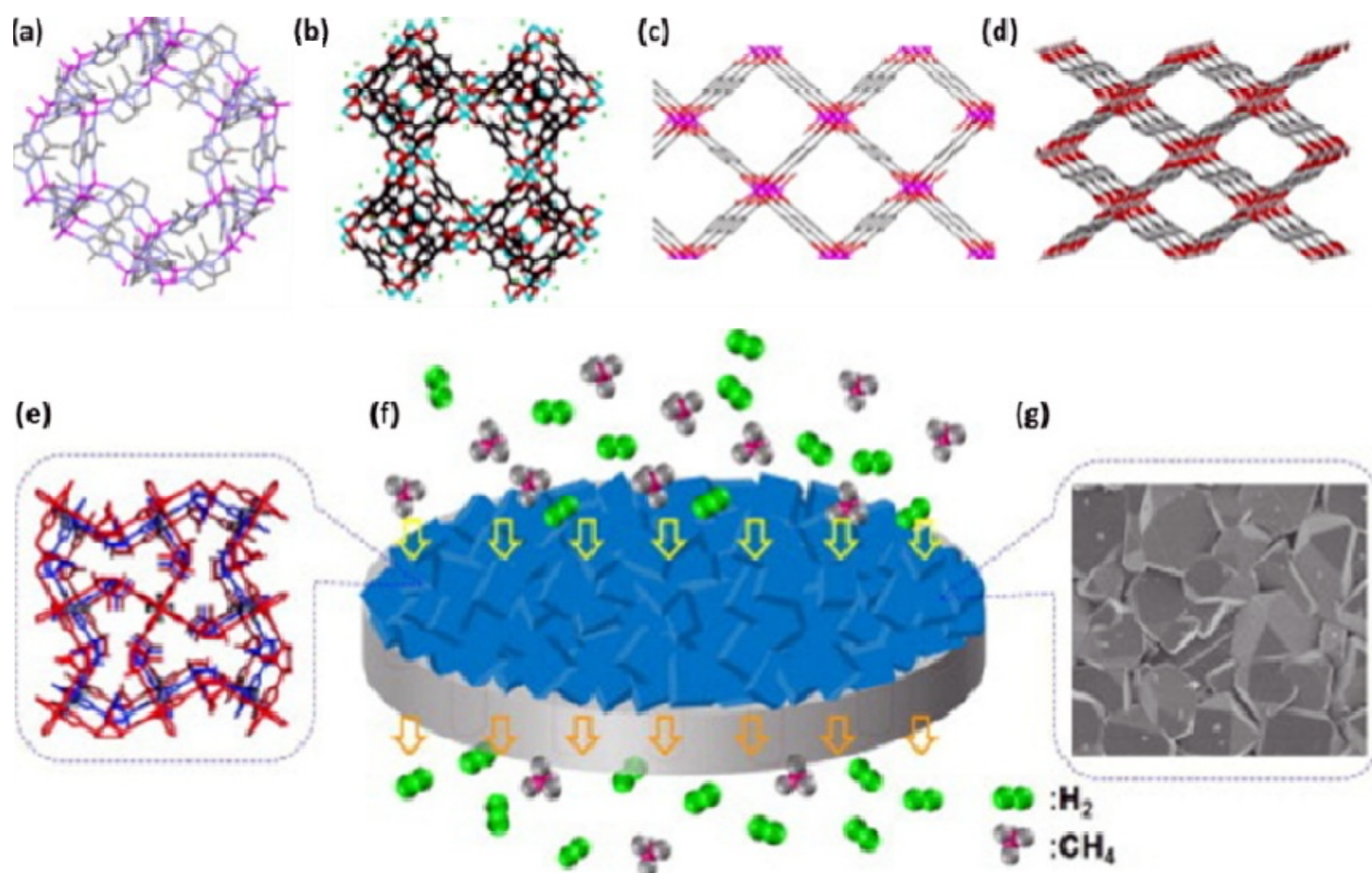
Fig. 2. Representation of the structures of the MOFs and schematic of gas separation by MOFs, see [45,49] for details. [45, 49]. (a)ZIF–8, (b)Cu$_3$(BTC)$_2$, (c)MIL–47, (d)MIL–53(Al),(e) Zn–CD, (f) schematic of gas separation by MOFs and (g) SEM image of Zn–CD crystal.
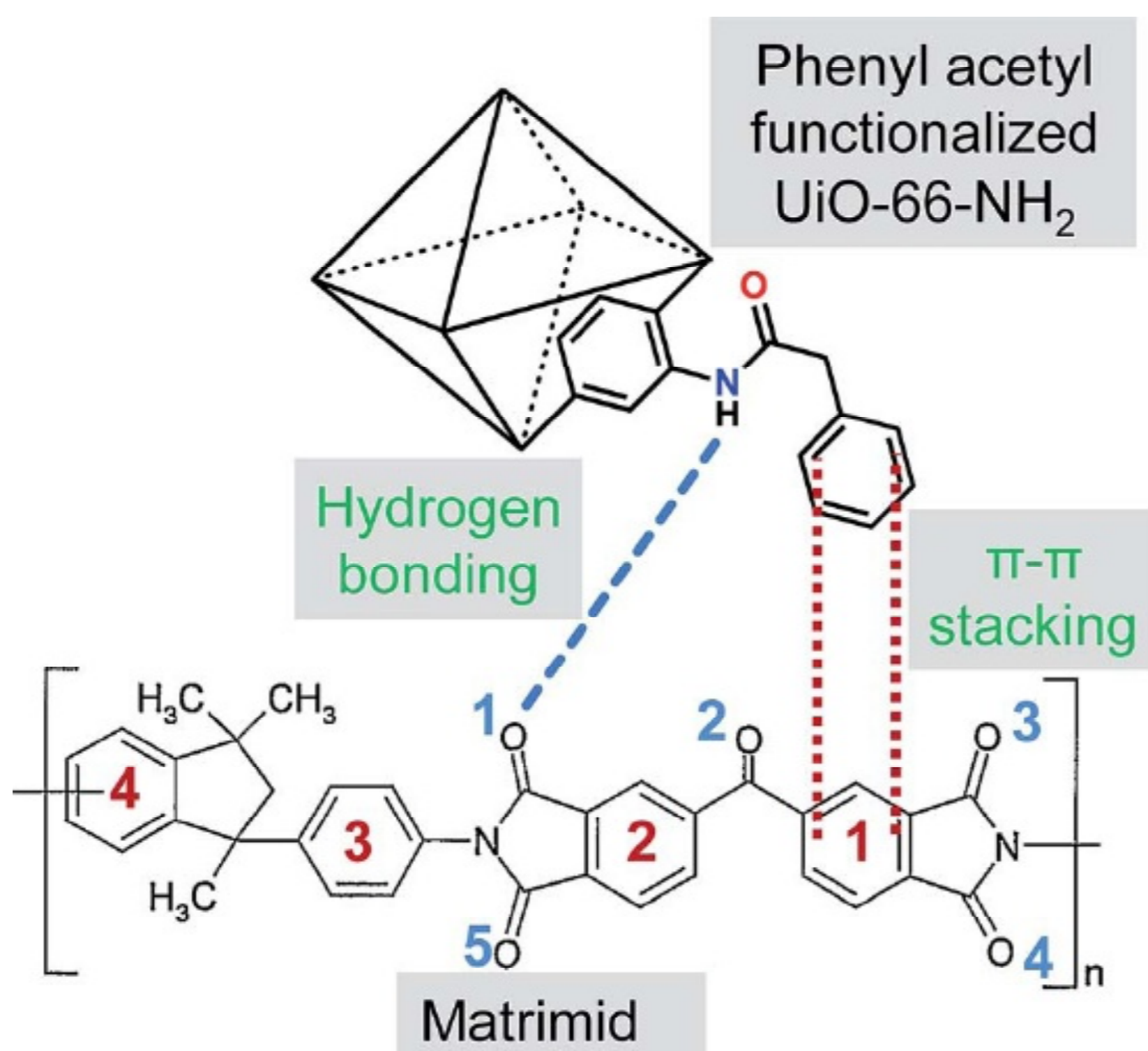

Fig. 3. Scheme demonstrating the favorable interactions between the Matrimid® polymer and phenyl acetyl functionalized UiO-66-NH$_2$ based on surface functionality, reprinted with permission from S. R. Venna, M. Lartey and T. Li // J. Mater. Chem. A **3** (2015) 5014, (c) 2015 The Royal Society of Chemistry.

erties. The results showed that the pure gas permeability (He, CO$_2$, CH$_4$, N$_2$, O$_2$) and the selectivity of gas pairs (He/CH$_4$, CO$_2$/N$_2$, CO$_2$/CH$_4$, O$_2$/N$_2$) for CuTPA mixed matrix membranes were improved over unmodified membranes. Basu *et al.* [49] incorporated four kinds of MOFs (ZIF–8, Cu$_3$(BTC)$_2$, MIL–47 and MIL–53(A1)) (Figs. 2a-2d) as fillers in PDMS

membranes. The membranes were applied in solvent resistant nanofiltration (SRNF). The membranes showed increased permeability but lower retention compared to unfilled membranes. Zn–CD membrane was synthesized by Kuang *et al.* [45] on porous ZnO support (Figs. 2e-2f) and used for gas separation. The single and binary gas permeations of the Zn–CD membranes were systematically investigated. The separation factors of H$_2$/N$_2$ and H$_2$/CH$_4$ gas mixture reached to 19.1 and 14.5, respectively, indicating these Zn–CD membranes would have great potential applications for hydrogen separation. Venna *et al.* prepared mixed matrix membranes with modified UiO-66-NH$_2$ based MOF particles as the dispersed phase and Matrimid® as the continuous matrix to ensure good adhesion with a polymer of choice and for fabricating MMMs with improved gas separation [50]. The aromatic groups present in the polymer are expected to interact favorably through π–π stacking with the aromatic ring of the –PA group and the imide groups in the polymer are expected to interact strongly with the –NH$_2$ groups and amide linkages through hydrogen bonding as shown in Fig. 3.

Moreover, CNTs have attracted more research introduced into a polymeric matrix to further improvement in performance, due to their small size, high length to diameter ratio, cylindrical structure and prominent mechanical, physical and chemical prop-

Table 1. Gas permeability and permselectivity of CA/C-MWCNTs MMMs at 2 bar pressure (reprinted with permission from A. Moghadassi, Z. Rajabi and S. Hosseini // J. Ind. Eng. Chem. **20** (2014) 1050, (c) 2014 Elsevier).

| Polymer-CNT loading | P (Barrer) | | S | | | | |
	He	N_2	CH_4	CO_2	CO_2/CH_4	CO_2/N_2	N_2/CH_4
CA/MWCNTs-0%	3.11	0.44	0.26	1.08	4.15	2.4	1.69
CA/MWCNTs-0.25%	20.24	0.48	0.31	6.53	21.06	13.60	1.55
CA/MWCNTs-0.45%	22.81	0.65	0.52	10.92	21	16.8	1.25
CA/MWCNTs-0.65%	25.36	0.89	0.63	13.74	21.81	15.43	1.41
CA/MWCNTs-0.85%	26.18	0.91	0.65	13.84	21.30	15.20	1.4
CA/MWCNTs-1%	26.19	0.97	0.66	14.21	21.20	14.65	1.47

erties. [Cellulose acetate (CA)-blend-multi walled functionalized carboxylic carbon nano tubes (C-MWCNTs)] mixed matrix membranes (MMMs) were prepared by Moghadassi *et al.* and had better gas permeability and gas pair selectivity performance, shown in Table 1 [51].

2.2. Heat treatment

In order to change the membrane properties, the membrane material can be thermal treated at certain temperature for a period of time. The arrangement of the polymer molecules can be changed to enhance flexibility and degree of density of the membrane. Because of the difficulty in grasping the heat time for the modification, fewer reports related this topic exists. He *et al.* [52] carried out the heat treatment of the PVDF membrane at 393.2K for 12 min. After the heat treatment, the number of carbonyl (C=O) and hydroxyl(C–OH) on the membrane surface increased, that is to say, the surface polarity of the membrane was enhanced. Correspondingly, the separation property was significantly improved.

3. CHEMICAL MODIFICATION

3.1. Group substitution

Group substitution of polymeric gas separation membranes provides potential solution to improve the gas separation performance, thus surpassing the "upper–bound" limit of the permeability–selectivity relationship. It include samination [53], bromination [54], sulfonation [55], benzoylation [56], and so on [57].

Taking PPO (Fig. 4a) modification as example, in order to further improve the gas separation performance, chemical modifications on the surface of PPO membrane had been done. Cong *et al.* [28] synthesized brominated poly(2,6–diphenyl–1,4–phenylene oxide) (BPPO, Fig. 4b) as a new membrane material for gas separation with higher CO_2 permeability (78 Barrer) and selectivity. Bhole *et al.* [53] showed that the substitution by either nitro or amino group on PPO (Fig. 4c), increased the chain stiffness and packing density and lowered thermal stability in comparison to unsubstituted PPO. Hamad *et al.* [54] had studied brominated PPO (PPOBr,
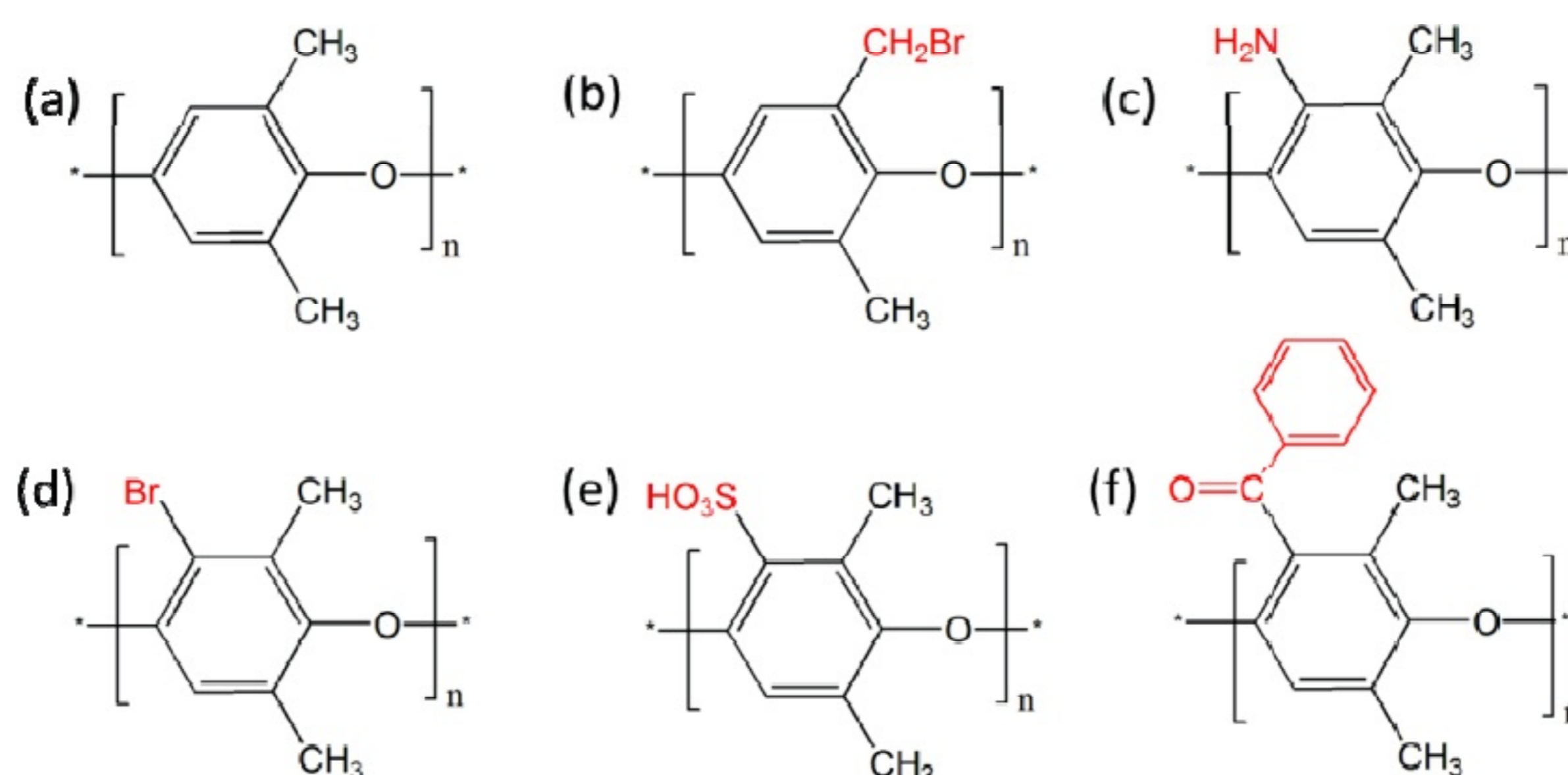
Fig. 4. Structure of chemical modified PPO: (a) PPO; (b) BPPO; (c) PPO-NH$_2$; (d) PPOBr; (e) sulfonated PPO; (f) benzoylated PPO.
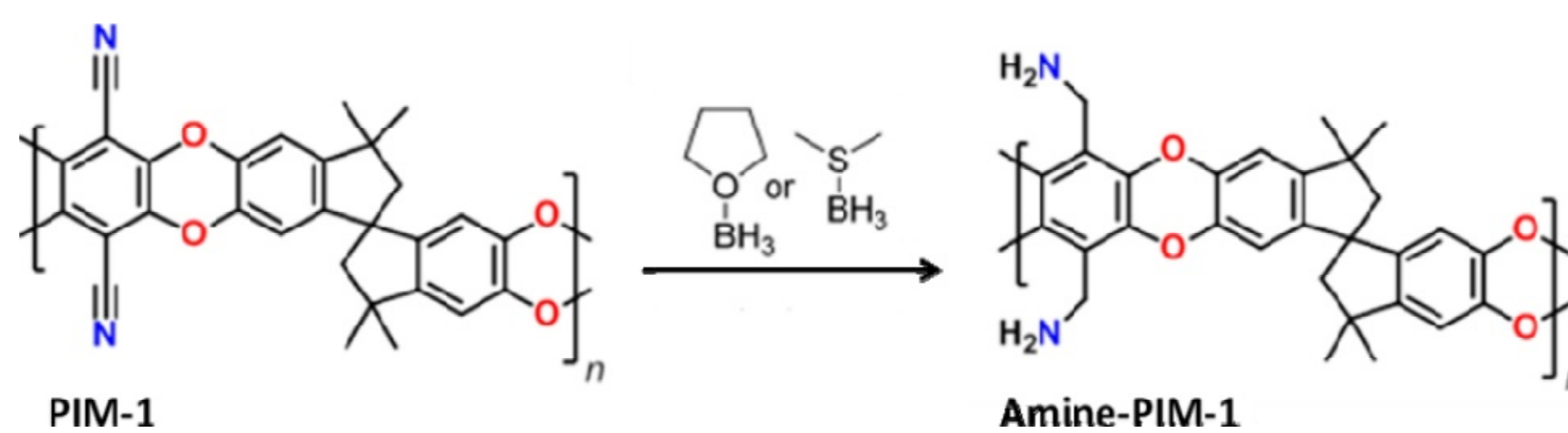
Fig. 5. Amine post-Modification of polymers of intrinsic microporosity (PIM), reprinted with permission from C. R. Mason, L. Maynard-Atem, K. W. Heard // Macromolecules **47** (2014) 1021, (c) 2014 American Chemical Society.
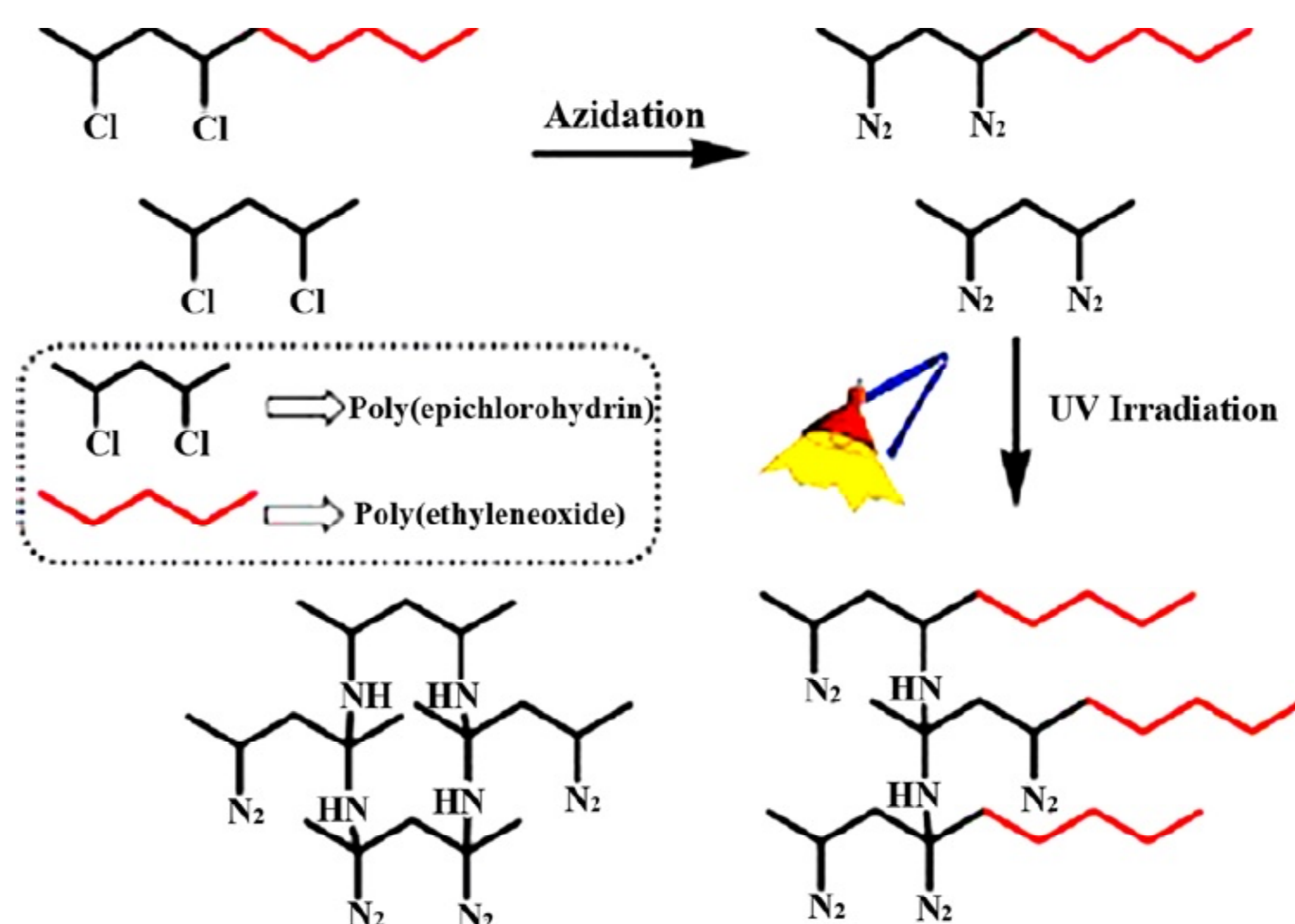

Fig. 6. The mechanism of UV cross–linking of azidatedhydrin polymers, reprinted with permission from B.N. Gacal, V. Filiz, S. Shishatskiy // J. Membrane Sci. **467** (2014) 126, (c) 2014 Elsevier.

Fig. 4d) with high molecular weight. The gas permeability between brominated PPO and un–brominated PPO is different. The former membrane has higher permeability. In order to further improve the performance of the brominated PPO, the brominated PPO was further sulfonated (SPPOBr). A study showed the SPPOBr membranes had higher gas permeability and lower gas permeability ratio than sulfonated PPO (SPPO) (Fig. 4e), and lower gas permeability and higher gas permeability ratio than brominated PPO. These effect are believed to be the direct result of the manipulation in the polymer backbone stiffness, membranes density and packing, and free volume fraction [55]. Bhole *et al.* [56] investigated the benzoylation of PPO (Fig. 4f), they showed that the benzoylation substitution on PPO led to the increase of T_g and decrease of thermal stability and gas permeablity.

Besides, Nitrile groups in the polymer of intrinsic microporosity PIM-1 (The archetypal membrane-forming PIM, referred to as PIM-1, Fig. 5) were reduced to primary amines using borane complexes by Mason and showed higher CO_2 uptake and higher CO_2/N_2 sorption selectivity for amine"PIM-1 membrane [58].

3.2. Cross–linking

The cross–linking of polymeric membranes may be a wise way to balance between permeability and selectivity [59]. Cross–linking modification can be realized by UV irradiation [60], chemical reaction [61,62], grafting [63], blocking [64], and so on.

Using a cross–linking strategy, the time–dependent gas transport properties of thin polyarylate films are examined by McCaig and co–workers [65]. The results showed that cross–linking led to a substantial gain in selectivity, and slowed the rate of physical aging compared with non–crosslinked thin films. An ultra–thin polyimide separation layer was prepared through the UV cross–linking by Marek and co–workers [60]. The crosslinked membranes were difficult to dissolve in the solvent like DMF and THF. The ultra–thin polyimide layer with poly(phenylene oxide) as substrate had good gas separation and high permeation rates. After UV cross–linking and azidation, the selectivities of CO_2/CH_4 and H_2/N_2 on polyepichlorohydrinhomo polymer (H–hydrin) and poly(ethyleneoxide–ran–epichlorohydrin) copolymer (C–Hydrin) (Fig. 6) were increased [66].
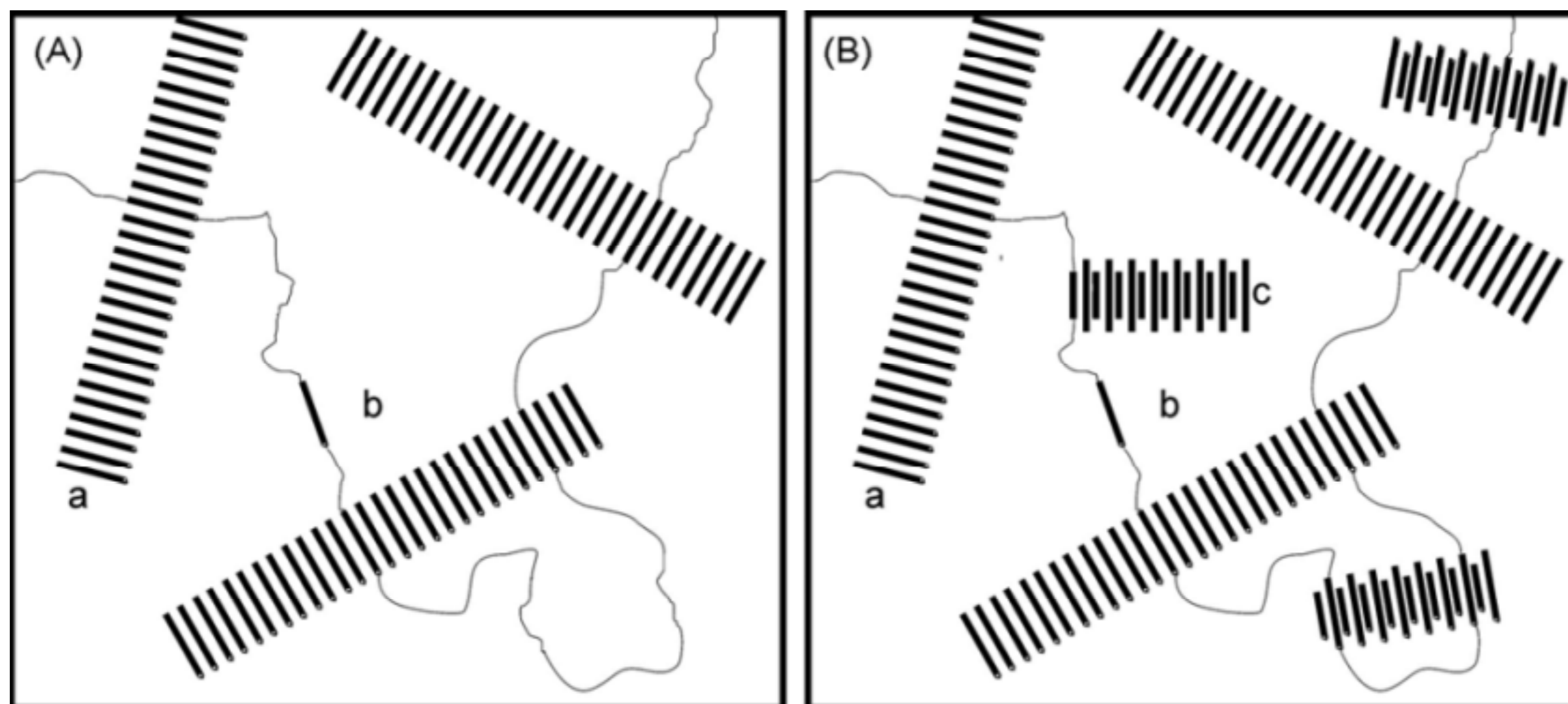
Fig. 7. Cartoon of a PEO containing segmented block copolymer with crystallized hard segments of monodisperse length and PEO segments are either fully amorphous (A) or semi–crystalline (B). (a) Crystalline hard segment; (b) amorphous PEO phase with non–crystallized hard segment; (c) crystalline PEO, reprinted with permission from D. Husken, T. Visser, M. Wessling // J. Membrane Sci. **346** (2010) 194, (c) 2010 Elsevier.

Cross–linking by chemical reaction is one of the most common methods. By immersing the 6FDA–durenefilms in a diaminobutane dendrimer solution, Shao *et al.* [59] cross–linked 6FDA–durene films with a series of novel multi–functional groups, improved the gas separation performance of polyimide membranes, especially for H_2/N_2, He/N_2, H_2/CO_2 and shown the potential to surpass the gas separation performance set by the traditional permselectivity–permeability trade–off line.

3.3. Co–polymerization

The grafting and blocking co–polymerization methods have been adopted to modify various membrane materials, such as polyolefin, polysulfone, PET, polycarbonate, SBS, and polyacrylonitrile. Freger *et al.* modified polyamide thin–film composite membrane using grafting of a hydrophilic polymer onto the membrane surface to improve its fouling properties [63]. Changing the soft segment length to control the chain flexibility is also a useful way to modify the performance of the membranes. However, the grafting density cannot be exactly controlled and grafting modification effect is closely related to the grafting density. If grafting density is too high, the nano–sized pores on the membrane surface are easy to be blocked, leading to loss of membrane separation performance. Three poly(acrylonitrile–*co*–maleic acid) (PANCMA) copolymers were prepared and grafted with PEG (PANCMA–*g*–PEG) by Nie and co–workers [67]. The results demonstrated grafting PEG was effective to improve the performance of the membranes. In addition, the antifouling properties of PANCMA membrane were enhanced obvi-

ously by the immobilization of PEG on membrane surface. Husken *et al.* [64] prepared poly(ethylene oxide)–based segmented block copolymers containing monodisperse amide segments for the CO_2 permeation (Fig. 7). The gas permeability and the gas transport values were dependent on both the dispersed hard segment concentration and the polyether segment length. Amooghin *et al.* used 3-aminopropyl(diethoxy)methylsilane (APDEMS) as the silane coupling agent The defect free polymer/filler interface was achieved by the aminosilanes grafted on the external surface of the zeolites.

3.4. Ionic liquid modification

Ionic liquids are molten salts which are made of cations and anions [68-70]. Ionic liquids as modifiers to enhance the performances of gas separation membranes have attracted many researchers' attention in recent years. For example, as shown in Fig. 8, different ionic liquid groups modified PPO (BuIPPO, MeIPPO, PyIPPO and TrIPPO) membranes were prepared by Cong and co–workers [16]. They found that the CO_2 solubility of the IPPO was better than the pure PPO and the PyIPPO had the best CO_2/N_2 separation performance among the four IPPOs. Amphiphilic graft copolymers consisting of poly(vinylchloride) (PVC) main chains and polymerized ionic liquid (PIL) side chains were synthesized via atom transfer radical polymerization by Chi *et al.* [71]. Upon utilizing a PVC-g-PIL/IL composite with 15 wt.% IL, the CO_2 permeability increased to 137.6 Barrer by approximately 7.7-fold with a moderate decrease of selectivity, Fig. 9.
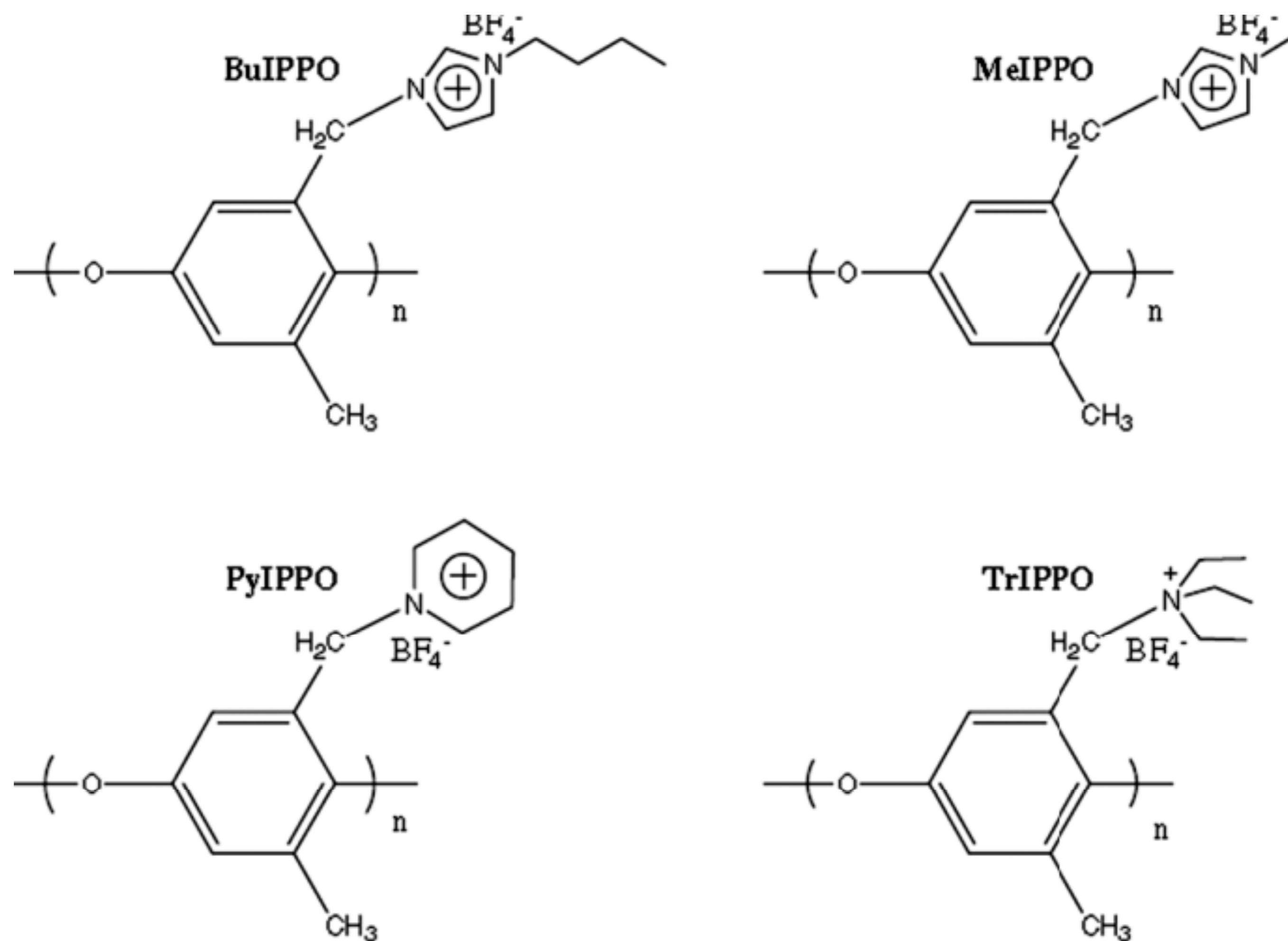
Fig. 8. Structural illustration of IPPO, reprinted with permission from H. Cong, B. Yu, J. Tang // J. Polym. Res. 19 (2012) 1, (c) 2012 Springer.
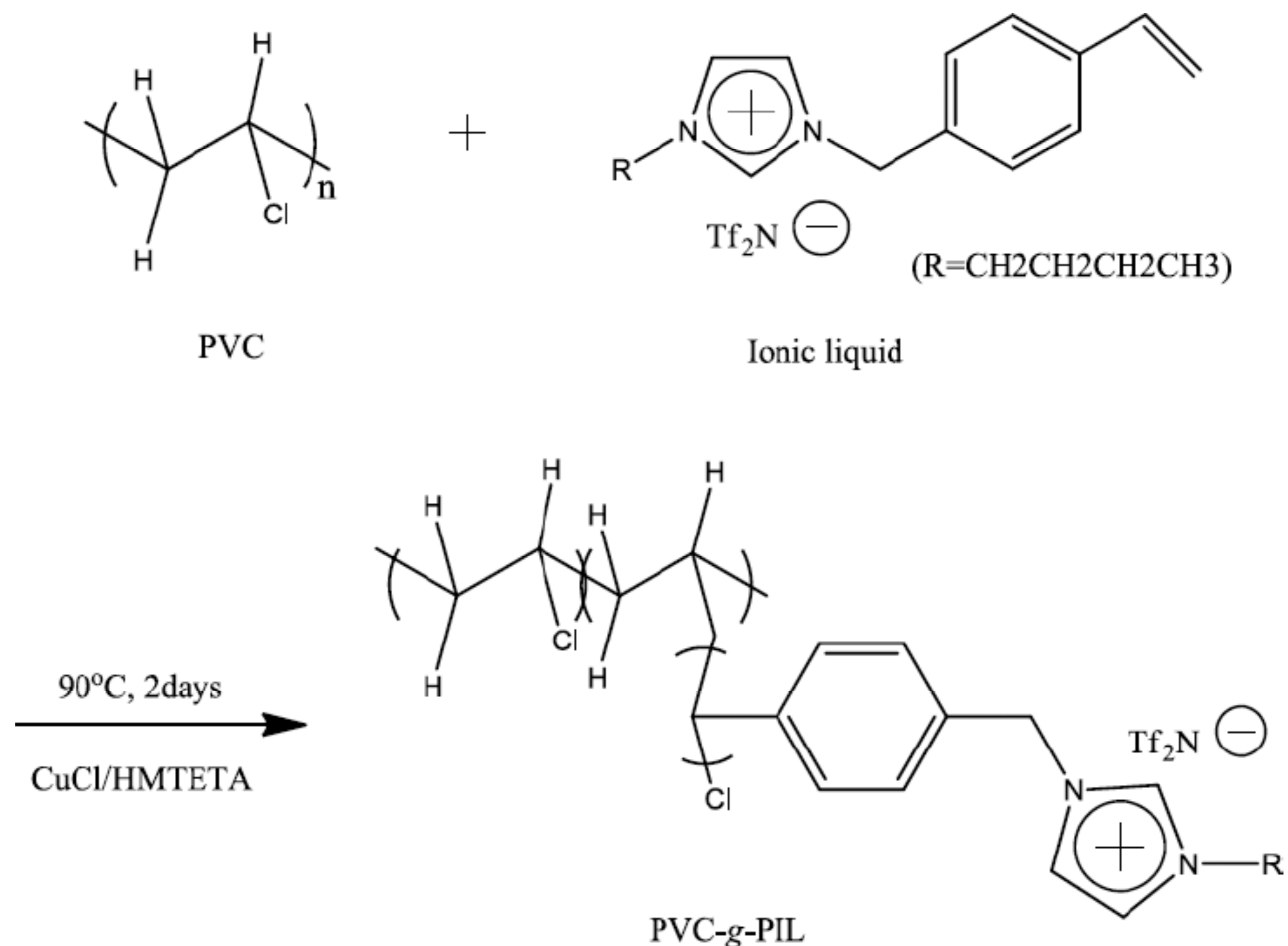

Fig. 9. ATRP synthesis of PVC-g-PIL graft copolymers, reprinted with permission from W. S. Chi, S. U. Hong, B. Jung // J. Membrane Sci. **443** (2013) 54, (c) 2013 Elsevier.

3.5. Plasma surface modification

Although there are many ways to alter the surface chemistry properties of polymer membrane, plasma treatment appears to be one of the most effective and convenient one. Recently, low–temperature plasma techniques have been used to prepare highly selective composite membranes for gas separation, because plasma treatment can adjust the degree of the modification. Borisov *et al.* [72] carried out the surface fluorination of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and poly(vinyl trimethylsilane)

(PVTMS) films. The control of the fluorine atom density in the discharge and density of fluorine atoms flux on the modified surface was used to increase their selectivity in gas separation. It was found that molecular sieving was the dominant mechanism for gas separation.

3.6. Other methods

Wholly aromatic hyperbranched polyimides for gas separations were prepared by condensation polymerization reaction of dianhydrides and a triamine monomer, tris(4-aminophenyl)amine [73]. Interfacially polymerized polyamide thin film composite membrane was modified by electrostatic self–assembly of polyethyleneimine on the membrane surface by Zhou et al. [74] The same method had been used by Meier–Haack and Müller to adsorb polyelectrolyte multilayer systems on the polypropylene flat sheet membrane [75].

4. GAS SEPARATION PROPERTIES

Polymeric membranes in the different states have different properties. In general, in the rubbery state, the polymeric membranes show high gas permeability. In the glassy state, polymeric membranes have good mechanical properties and high selectivity. For example, PDMS is a rubbery silicone polymer and extensively used to remove different solvents from air or nitrogen. Although the permeability coefficient of PDMS is larger, the selectivity of PDMS is very poor. It is difficult to meet the requirements for industrial application. Many modification methods were used to improve the property of PDMS membranes. For instance, PDMS/silica nanocomposite membranes were prepared which overcame the trade–off between permeability and selectivity by enhancing both of them [76]. A PDMS/PES composite membrane was synthesized by Sadrzadeh and co–workers [77]. The sorption and permeation of C_3H_8, CO_2, CH_4, and H_2 through the synthesized composite membrane increased a lot.

Polyimide (PI) has attracted much attention for high gas selectivity, excellent thermal stability, high chemical resistance, good mechanical properties and outstanding electrical properties. Polyimide has been applied to a wide range of industries [78]. PI membranes can possess better properties by modification [79]. Copolymerization is an important modification method for polyimide. The copolymerization can be used to prepare composite membranes by synergistic combination of different functions materials [80] [80]. Through copolymerization, PI membranes can possess more excellent properties. For example, copolyimide membranes with different polyethylene oxide (PEO) content exhibit higher permeability coefficients for CO_2 [81]. Tena et al. [82] reported a poly(ether–co–imide)s with approximately 45% weight of polyether in the final copolymer presents good gas separation properties. On the basis of the copolymerization, fluorinated poly(ether–co–imide)s showed an excellent separation performance for O_2/N_2 gas pair which eventually surpassed the present upper boundary limit [83]. In a carbon nanotube modified polyimide nanocomposite membranes, the permeability of O_2, N_2, and CH_4 increased with an increase of the carbon nanotube amount in the polymer matrix [84].

Besides water solubility, chemical stability, non–toxicity and biodegradability, PEO possesses a remarkably high CO_2/H_2 solubility selectivity because of its polar ether oxygen group [85]. The molecular weight and crystallinity are two key factors to the gas transport behavior. PEO with a high molecular weight and crystallinity has low gas permeability, but PEO with a low molecular weight and crystallinity is difficult to be directly used as gas separation membranes. Therefore, PEO–containing copolymer membranes have been widely used. The synthesized PTT–b–PEO copolymer presents good mechanical, thermal and processing properties [86]. Moreover, preparation of cross–linked organic–inorganic hybrid membranes is a useful way to improve properties of PEO. PEO/SiO$_2$ hybrid membranes made by Shao and co–workers show excellent CO_2/H_2 selectivity with the increase of the silica content [87]. In addition, cross–linked PEO containing –OCH_3 end groups would increase polymer fractional free volume, and thus exhibited high CO_2 permeability and CO_2/H_2 selectivity [88].

Polybenzimidazole (PBI) as a kind of gas separation membrane material possesses remarkable thermal, mechanical and chemical stability and superior physical, thermal and chemical stability at harsh operating conditions. Because of the relatively high chain packing density, PBI also has some disadvantage, such as limited solvent solubility [89]. PBI–silica hybrid membranes were prepared by Sadeghi and co–workers to enhance the gas separation properties of polybenzimidazole membranes [89]. The permeability of the condensable CO_2 and CH_4 gases were enhanced, whereas the permeability of the non–condensable N_2 gas significantly decreased upon increasing the silica content in the nano–composite membranes, because the increase of the silica content results in an increase in the solubility and a corresponding reduction in the diffusivity of the gases through the membranes.
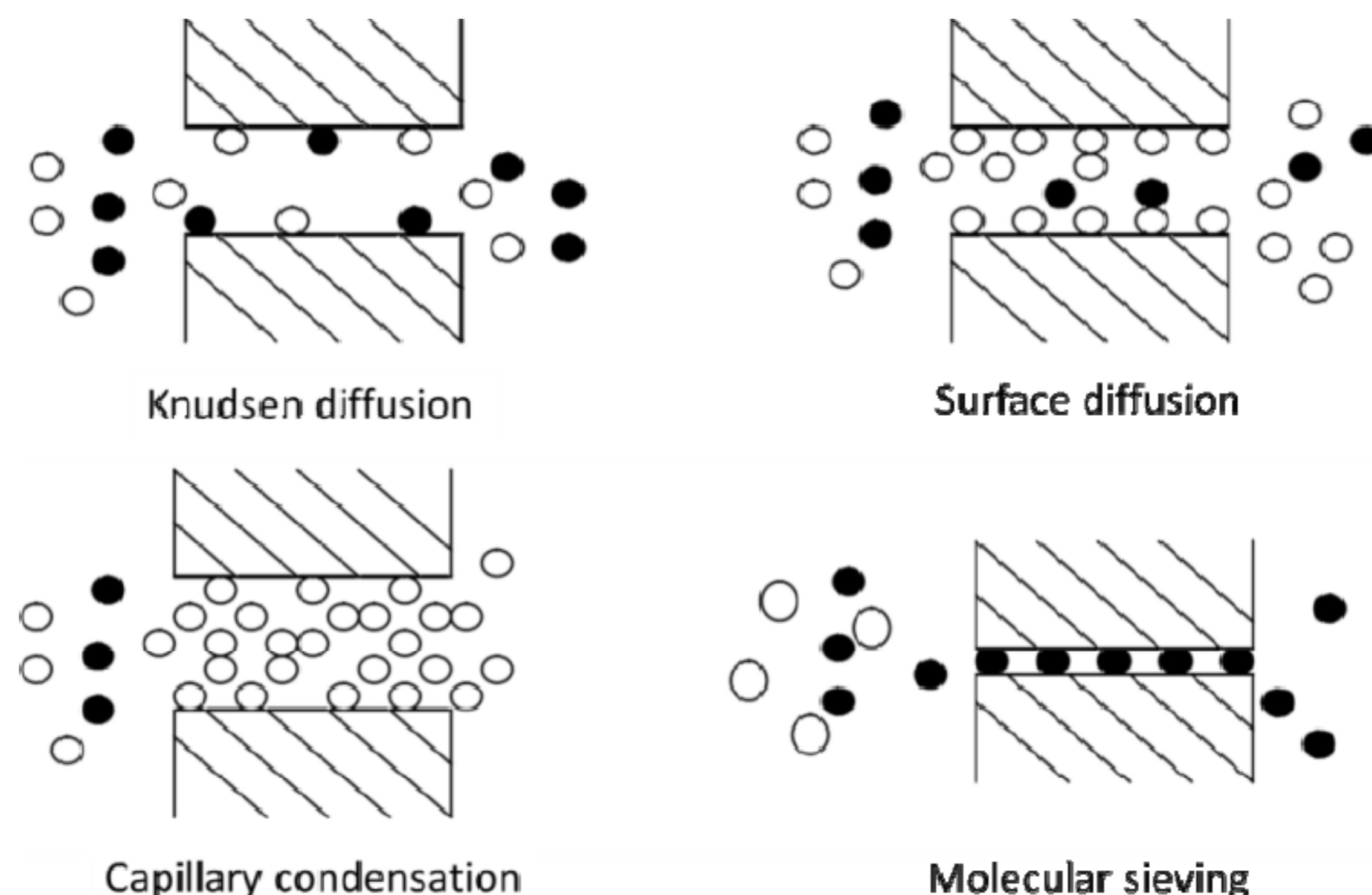
Fig. 10. Gastransport mechanism through microporous membrane, reprinted with permission from H. B. T. Jeazet, C. Staudt and C. Janiak // Dalton T. **41** (2012) 14003, (c) 2012 The Royal Society of Chemistry.

Based on Kumbharkar's research, the modified PBI membrane could achieve high thermal stability and good solvent solubility, implying its potential application as gas separation membrane materials. The occurrence of permeation characteristics (especially P_{H2} and P_{H2}/P_{N2}) near Robeson's upper bound [90].

After modification, great improvements in gas separation properties have been achieved in other polymer membranes such as PMMA, polyurethane and polysulfone [91-95]. The Robeson proposed a trade–off limitation between permeability and selectivity in polymeric membranes. Through these years' research, enhancement of desirable properties of polymeric membranes has overcome this shortcoming. The membranes which not only possess low weight, operational flexibility, compactness and low energy–consumption, but also overcome poor balance between permeability and selectivity will be widely used. With continued efforts, more excellent polymeric membrane for gas separation will emerge.

5. GAS TRANSPORT MECHANISM

Gas transport mechanism of modified polymeric membrane has great relation with membrane morphology. According to the gas transport mechanism, the membrane can be organized into three categories: porous polymer membrane, dense polymer membrane and polymer–inorganic membrane.

5.1. Porous polymer membrane

For porous gas separation membrane, the differences of the inner aperture surface properties makes interaction between gas molecules and the porous

medium different in a degree, this leads to the different transport characteristics. Gas transport mechanism in porous membrane mainly includes Knudsen diffusion and surface diffusion, capillary condensation, molecular sieving (Fig. 10) [17].

Knudsen diffusion

When the pore diameter of porous membrane film is much smaller than the mean free path of gas molecular, the collision probability between gas molecule and pore wall is greater than that between gas molecules [96]. Thus, the gas flow in the pores is dependent on the collision probability between gas molecule and pore wall, the process of gas flow throughout pores belong to Knudsen diffusion. For gas separation by Knudsen diffusion, the diffusion coefficients (D) will vary inversely with the square root of the molecular weight (M) of the gas as Eq. (1):

$$a_{i/j} = \frac{D_i}{D_j} = \sqrt{\frac{M_i}{M_j}}. \tag{1}$$

Surface diffusion

If the gas molecules were adsorbed on the porous wall, the gas molecules will move along the porous wall surface, thus generate surface diffusion flow. Adsorption is divided into chemical adsorption and physical adsorption. On one hand, when the adsorption is physical adsorption, the mobility of gas molecules will need lower energy. On the other hand, when the adsorption is chemical adsorption, the gas molecules could jump from one point to another point, though they tend to stick on the specific location steadily.

Capillary condensation

When the physical adsorption of gas components takes place on the membrane surface, and the capillary condensation effect occurring at the same time, this will gradually block the pores [96]. As the condensate flows through the porous channel and evaporates away from membrane surface, the separation of gas components can come true. Nevertheless, there are still two problems needing be paid attention to. Firstly, capillary condensation will not come up until the surface tension exists in the experimental circumstance. Secondly, it is difficult to observe the capillary condensation effect.

Molecular sieving

When the membrane is contacted with the gas molecules with different sizes, the smaller sized molecule will be admitted to pass, and the bigger sized molecule will be intercepted. If the pore size of the membrane matches the size of gas molecules. Consequently, the gas separation could come true. Frequently, the molecular sieving is based on the size of gas molecule, so this mechanism can provide favorable flux and selectivity. It has been proved to be an ideal method to separate the gas molecules.

5.2. Densepolymer membrane

Gas transport through a dense polymeric membrane can be mathematically described. But the description is always complex, especially after the modification of polymeric membranes. To predict the permeation of gas species through dense polymeric membranes, several models are given in the literatures, as described below.

Solution–diffusion model

Solution–diffusion model based on solution and diffusion through the bulk polymer is widely accepted to be the main transport mechanism of polymeric materials, firstly proposed by Thomas Graham [97]. Diffusivity–based gas separation mechanism is generally employed for chemically similar species like O_2 and N_2, where separation occurs due to the preferential permeation of the smaller species. The gas transport is as following: first, the gas adsorbs on the surface of membranes, then diffuses into membranes which is mainly driven by the concentration gradient, finally, desorbs on the other side of membranes. Based on Fick's first law [98], the diffusion flux of gas through the membrane J_i can be expressed by Eq. (2):

$$J_i = -D_i \frac{dC_i}{dx} = \frac{D_i}{i}\left(C_{i,0} - C_{i,l}\right),\tag{2}$$

where D_i is diffusion coefficient; dC/dx is theconcentration gradient of the gas across the membrane; $C_{i,0}$ and $C_{i,l}$ are the concentration of the gas on the upstream and downstream ends, respectively, and l is the thickness of the membrane.

In this model, the selectivity can be viewed as a function of differences in both the diffusivity and solubility coefficients of the two gases. Separation factor $a_{i/j}$ can be calculated by Eq. (3):

$$a_{i/j} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{S_i}{S_j},\tag{3}$$

where P is permeability of the gas and defined as $P = DS$; D is the diffusion coefficient and S is the solubility coefficient. In fact, most membrane systems for gas separation in operation are diffusivity–based. However, in certain industrial and environmental applications, it is preferable to achieve separation based on solubility difference [99].

Free volume model

The free volume theory is first applied in membrane diffusion process by Fujita [100], and this model can describe the relationship between diffusion coefficient and concentration of organic vapor in the colloidal polymer. The gas permeability depends on the free volume of polymeric membrane. The generation of free volume comes from the non–close packing of polymer. The diffusion coefficient D_T can be calculated by the equation in the following Eq. (4):

$$D_T = RTA_i \exp\left(-\frac{B}{v_f}\right),\tag{4}$$

where A_f depends on the size and shape ofpenetration molecular; B relates to the minimum local free volume and v_f is free volume fraction. Furthermore, an improved Fujita model was proposed by Frish and Stern to remove some deviation [101], and Ganesh expanded the free volume model to make it suitable for gas transport in glassy polymer [102].

Doal adsorption model

Doal adsorption model assumes that the gas soluble in glassy polymeric membranes has two kinds of different adsorption: one is dissolved in the polymer solution and the solute molecules follow Henry's law; the other is adsorbed in the micropores of polymer and this part of the soluble molecules follow Langmuir's law [103]. The Langmuir mechanism evidently arises from the non–equilibrium nature of the glassy state [104]. The solubility C is the sum of the solution and adsorption, can be calculated by Eq. (5):

$$C = C_{i,H} + C_{i,L} = k_{i,H}F_i + \frac{C'_{i,L}b_iP_i}{1+b_iP_i}, \tag{5}$$

where $C_{i,H}$ and $C_{i,L}$ are the gas *i* solute concentration followed Henry's law and Langmuir laws, respectively; $k_{i,H}$ is Henry coefficient; P_i is the partial pressure of gas *i*; $C'_{i,L}$ is Langmuir volume coefficient and b_i is affinity constant for the hole and gas *i*. Doal adsorption model needs to consider the relationship between diffusion coefficient and concentration. However, such improvement needs to introduce parameter, therefore making the transfer mechanism complicated. In addition, the parameters of Doal adsorption model are not directly associated with chemical structure of polymer, which will limit the application of this model.

5.3. Polymer–inorganic membrane

Inorganic nanoparticles are widely used to modify polymeric membranes via blending method. After modification, inorganic materials will often disrupt the accumulation of polymer matrix chain, increase the free volume of polymer, and thus improve the gas molecular diffusion in the membrane. Meanwhile, the transport properties of organic–inorganic hybrid membranes are strongly dependent on the nanoscale morphology of the membranes. In particular, the morphology of the interface is a critical factor to determine the overall transport properties. Gas molecule transfer mechanism in the mixed matrix membrane is more complicated. As a result, many transfer mechanism theories of mixed matrix membrane have been proposed [1].

Maxwell model
In Maxwell model, filling particles added to the polymer typically reduce the permeability coefficient of the gas. Because the filler particles will first occupy the space of polymer and reduce the adsorption of original polymer, thereby reduce the solubility of the gas molecules in the membrane; Secondly, filling particles also increase the twist degree of the gas molecular diffusion path, eventually led to the decrease of the permeability [105,106]. The shortcoming of the Maxwell model is that it ignores the interaction between the filler particles and polymer chain segment, which can significantly change the gas molecular diffusion coefficient and the solubility [107].

Free volume theory and solubility theory
In traditional filled systems, flexible rubbery polymer chains mix with nanoscale particles without increasing free volume in the polymer phase, resulting in a more tortuous diffusion path, smaller cross–sectional area available for transport, and consequently reduced permeability. Freeman *et al.* [108] thought smaller particles yield more polymer/particle interfacial area and provide more opportunity to disrupt polymer chain packing, which will affect molecular transport. Gomes *et al.* [109] showed that nanoparticles will not only disrupt the accumulation of polymer chain segment and are likely to occupy the free volume of polymer, so the performance of matrix membrane is the result of a combination of the above two aspects. Solubility theory is based on the interaction between gases and filling particles. Filling particles with surface functional groups (such as hydroxyl) can interact with polar gases such as CO_2, SO_2, thereby increasing the solubility of gas in the mixed matrix membrane, thus improving the permeability of the gas [110].

Nanogap theory
Nanogap theory is based on the poor compatibility between the inorganic particles and the polymer matrix chain segment. Due to the poor compatibility of the inorgainc surface and the polymer, the polymer chains do not tightly contact with the inorganic nanoparticle, thus forming an arrow gap surrounding the silica particles (Fig. 11). The gas diffusion path is shortened, and thus the apparent gas diffusivity and permeability are increased [28]. Additionally, Moore and Koros [111] observed the generation of interface gaps in the Matrimid®/zeolite 4A composite membranes.

6. CONCLUDING REMARKS

From beginning, gas separation membranes are an interdisciplinary field. Most importantly, the membrane industry itself has a profound perspective as it is illustrated by the growth rates, the steadily in-
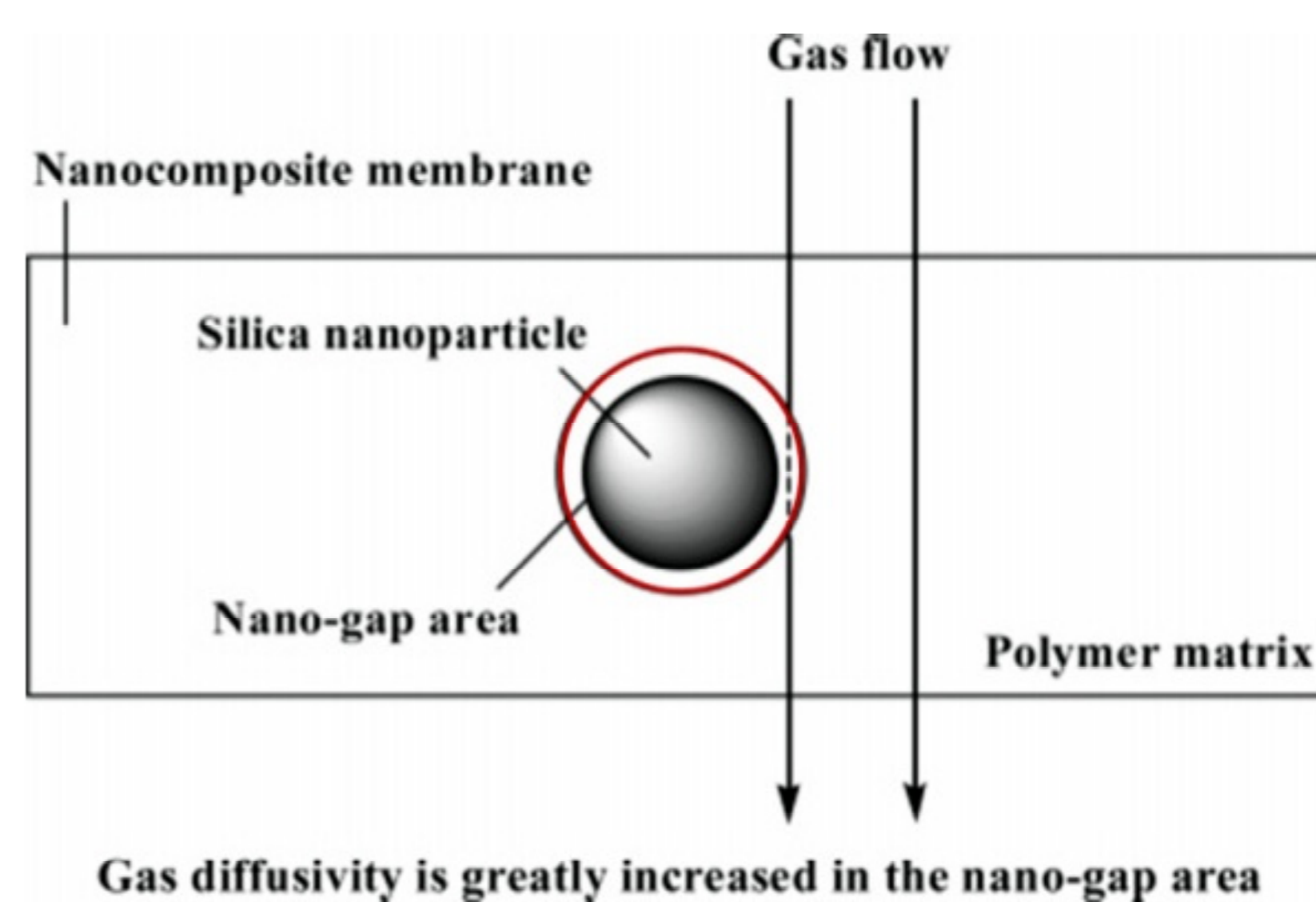

Fig. 11. Nanogap theory transport mechanism through microporous membrane, reprinted with permission from H. Cong, X. Hu, M. Radosz // Ind. Eng. Chem. Res. **46** (2007) 2567, (c) 2007 Elsevier.

creasing diversity of applications, and the growing number of technically feasible membrane processes. Next generation membranes for gas separation will have more function with better performance. On one hand, polymeric membranes are promising membranes for gas separation. On the other hand, many modification methods have been investigated to enhance the separation performance and physical properties of polymeric membranes. Further study should focus on the synthesis of hybrid/composite polymeric membranes with better selectivity and permeability, the exploration of gas transport mechanism of polymeric–based membranes with special structures, and investigation of structure and property of polymeric membranes in nano and molecular scales. Chemists, physicists and material scientists' collaborative efforts are particularly desirable in this field. Through multidisciplinary endeavors, more and more polymeric membranes with fascinating properties will emerge soon and hold great promise in the future.

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