

Improvement of CO₂/CH₄ separation characteristics of polyimides by chemical crosslinking

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Abstract

Uncrosslinked and crosslinked polyimides and copolyimides have been synthesized in order to increase selectivity without an unacceptable loss in permeability. The goal was to reduce undesirable effects caused by CO₂ induced swelling in CO₂/CH₄ separation processes by stabilizing the polyimide structure with crosslinks. In the polymerization reaction 6FDA (4,4'-(hexafluoroisopropylidene)diphthalic anhydride) was used as dianhydride monomer and *m*PD (*m*-phenylene diamine) and DABA (diamino benzoic acid) were used as diamine monomers. With copolyimides containing strong polar carboxylic acid groups (i.e. 6FDA-*m*PD/DABA 9:1) reduced plasticization was seen up to a pure CO₂ feed pressure of 14 atm, presumably due to hydrogen bonding between the carboxylic acid groups. By chemical crosslinking of the free carboxylic acid groups of the 6FDA-*m*PD/DABA 9:1 with ethylene glycol, the swelling effects due to CO₂ can be reduced at least up to a pure CO₂ feed pressure of 35 atm. With increasing degree of crosslinking, increasing CO₂/CH₄ selectivity was found because of reduced swelling and polymer chain mobility. By using ethylene glycol as a crosslinking agent, CO₂ permeability was not significantly lowered because the reduced chain mobility was compensated by the additional free volume caused by the crosslinks. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Gas separation by polymer membranes is a proven technology that has found a wide range of applications. Flexible design, the compactness and the efficiency of membrane units compared to conventional gas separation methods like cryogenic distillation or

absorption are particularly attractive [1–3]. In the area of CO₂/CH₄ separation with membranes, the removal of CO₂ in landfill gas recovery processes and CO₂ removal from fractured wells as well as the removal of CO₂ in enhanced oil recovery applications (EOR) are of interest. In some of these separation applications, the membranes are exposed to high CO₂ concentrations in the feed stream. The resulting strong interactions between the CO₂ and the polymer material often affects flux and permselectivity properties. In extreme cases, the gaseous feed stream can be composed of

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over 50% CO₂ at an elevated temperature and up to a feed pressure of 60 atm. These extreme operation conditions result in the swelling and plasticization of most membrane materials by the CO₂ present in the feed stream. For the application of membrane based gas separation in EOR processes, it is important to develop new membrane materials with reduced plasticization effects due to high CO₂ partial pressure. This study was undertaken to determine if swelling and plasticization of the polymer structure can be achieved by crosslinking.

One method for crosslinking membrane materials is the UV-irradiation of benzophenone-containing polyimides [4] or bisphenol A based polyacrylates [5]. This leads, especially in the separation of gas pairs with a large difference in molecular size, to a significant improvement of permselectivity. But simultaneously the permeability is decreased by crosslinking due to the strongly reduced chain mobility and to the increased packing density of the polymer chains. A disadvantage of photochemical crosslinked membrane materials is that the degree of crosslinking depends strongly on experimental conditions, i.e. irradiation time or the type of mercury lamp. Moreover, under the experimental conditions of UV-irradiation crosslinking reaction as well as photo-fries rearrangements are possible [5].

For this study simultaneous inhibition of chain mobility and intrasegmental packing by changes in backbone structure was of interest. Therefore, polyimides with strong polar associating functional groups as well as chemical crosslinked polyimides and copolyimides were synthesized. Permselectivity and permeability properties for the CO₂/CH₄ separation were investigated. 6FDA-based polyimides were used, because it is well known that introduction of –C(CF₃)₂– linkages restricts the torsional motion of neighboring phenyl rings and tends to enhance the permselectivity for the CO₂/CH₄ system [6–10]. With different 6FDA-based polyimides and copolyimides the influence of strong polar carboxylic acid groups in polyimides was investigated. The effects of such carboxylic acid groups, expected to lead to pseudo-crosslinked polymers due to hydrogen bondings, was investigated for CO₂/CH₄ separation. The permeation and separation properties of pseudo-crosslinked and truly chemical crosslinked polyimides, obtained by treatment of carboxylic acids containing polyimides

with ethylene glycol, were compared. Also the influence of crosslinking degree on swelling and plasticization effects due to CO₂ was studied up to 41 atm pure CO₂ pressure. For all synthesized polyimides and copolyimides, permeability and permselectivity were investigated for the common gas pairs O₂/N₂ and CO₂/CH₄ using pure gas feeds. Mixed gas experiments were also performed using 50:50 CO₂/CH₄ feed mixtures.

2. Background and theory

In one-dimensional diffusion through a flat membrane, the local flux N of a penetrant can be described by Fick's law as shown in the following equation:

$$N = -D \left[\frac{\partial C}{\partial x} \right], \quad (1)$$

where the diffusion coefficient, D , may be a function of local concentration, C [11]. The permeability coefficient P is generally defined as the flux N normalized by pressure and membrane thickness

$$P = \frac{N}{(p_2 - p_1)/\delta}. \quad (2)$$

Thereby, p_2 and p_1 are upstream and downstream pressures of the penetrants and δ is the membrane thickness. Permeation is a solution–diffusion process. Therefore, the permeability coefficient can be expressed as a product of an average diffusion coefficient D and a solubility coefficient, S [12]:

$$P = S \cdot D. \quad (3)$$

The solubility coefficient is determined by the condensibility of the penetrants, by the polymer–penetrant interactions and by the amount of excess volume existing in the glassy polymer. The diffusion coefficient, D , is a measure of mobility of the penetrants between the upstream and downstream conditions in the membrane. The diffusion coefficient D is determined by packing and motion of the polymer segments and by the size and shape of the penetrating molecules.

The permselectivity of a membrane for gas separations is characterized by a separation factor $\alpha_{A/B}$ defined in terms of the downstream (y) and upstream (x) mole fractions of two components A and B is given

in the following equation:

$$\alpha_{A/B} = \frac{y_A/y_B}{x_A/x_B}. \quad (4)$$

In cases where the downstream pressure is negligible, the separation factor $\alpha_{A/B}$ is equal to the ratio of permeabilities of the two gases A and B under mixed gas feed conditions as shown in the following equation:

$$\alpha_{A/B}^* = \frac{P_A}{P_B}. \quad (5)$$

The ideal separation factor $\alpha_{A/B}^*$ is a measure of the intrinsic permselectivity of a membrane material for mixtures of A and B. By substituting Eq. (3) in Eq. (5), the ideal separation factor can be split into two parts

$$\alpha_{A/B}^* = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B}, \quad (6)$$

where D_A/D_B is the diffusivity selectivity and S_A/S_B is the solubility selectivity.

3. Experimental

3.1. Materials

Fig. 1 shows the chemical structures of the 6FDA-based crosslinked and uncrosslinked polyimides and copolyimides synthesized. It was also possible to synthesize the 6FDA–DABA polyimide with free carboxylic acid groups in every polyimide unit, but the obtained membrane films were too brittle for the investigation of gas permeation properties. By crosslinking of the 6FDA–DABA with ethylene glycol, better mechanical strength was reached, so that permeation experiments were possible.

3.2. Characterization

The structures of the synthesized polyimides were proved by $^1\text{H-NMR}$. The aromatic protons of the polyimides and copolyimides appeared in the range 7.2–8.1 ppm, the carboxylic acid protons in non-crosslinked copolyimides, i.e. 6FDA–*m*PD/DABA 9:1 were found at 11.75 ppm, whereas the aliphatic protons belonging to the crosslinks appeared at 2.5 ppm. In the infrared spectroscopy for all synthesized poly-

Table 1

Glass transition temperature T_g and molecular weight distribution for different non-crosslinked polyimides synthesized

Polyimide	T_g (K)	M_w (g/mol)
6FDA– <i>m</i> PD	578	50 000
6FDA– <i>m</i> PD/DABA 9:1	643	64 000
6FDA–DABA	727 (decomposition)	Non-sol. in THF

imides, signals typical for the imide bond were found at wave numbers of 1780, 1710, 1380, 1130 and 719 cm^{-1} .

Table 1 shows the glass transition temperature and molecular weight distribution for the 6FDA–*m*PD, which was used as a reference substance, the uncrosslinked 6FDA–*m*PD–DABA 9:1 and the 6FDA/DABA. For T_g it was found that with increasing number of strong polar carboxylic acid groups the glass transition temperature increases. The 6FDA–DABA sample showed decomposition at 727 K. The crosslinked samples showed no T_g or decomposition up to 750 K.

3.3. Polyimide synthesis

All monomer materials were purified before the polymerization reaction. The 6FDA dianhydride was sublimed twice, the *m*PD diamine was recrystallized twice from toluene and the diaminobenzoic acid was recrystallized from methanol. The monomers were stored separately under high vacuum.

For the synthesis of the polyimides in this study, chemical imidization was performed. In a moisture free flask with nitrogen inlet and magnetic stirrer, the diamine monomer was dissolved in *N,N*-dimethyl acetamide (DMAc) and the 6FDA dianhydride dissolved in DMAc was added dropwise at room temperature. The 20–25 wt% solution was stirred 6–8 h. Thereby high molecular polyamic acids were formed. The imidization was performed by the dehydration of the polyamic acids by adding a large excess of triethylamine and acetic anhydride to the reaction mixture and stirring 2–3 h at 323 K and 10–20 min at 373–383 K. After cooling to room temperature, the highly viscous reaction solution was slowly poured into methanol. The precipitated polyimide was homogenized in a blender; filtered and washed several times with fresh methanol. The obtained polyimide was

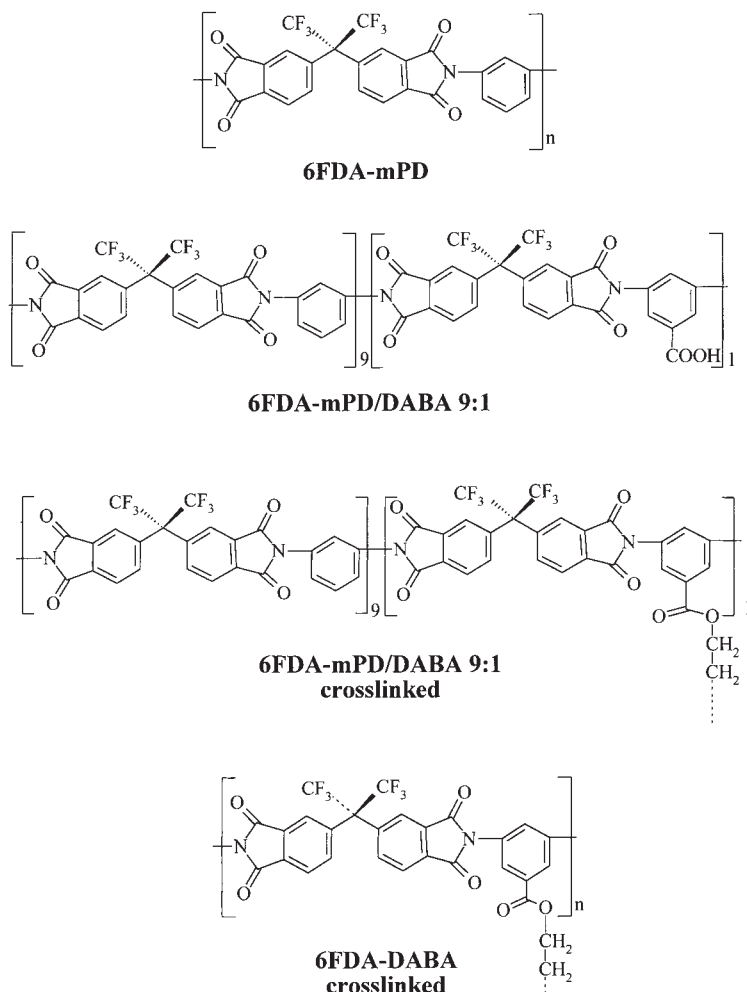


Fig. 1. Crosslinked and non-crosslinked 6FDA-based polyimides and copolyimides synthesized.

dried 12 h under vacuum at room temperature and at least 24 h under vacuum at 523 K.

3.4. Synthesis of crosslinkable copolyimides

Fig. 2 shows the reaction scheme of the synthesis of crosslinkable copolyimides. It is important to start with the less reactive diamine (DABA) in DMAc. The total amount of 6FDA is added to the diamine in order to form trimeric 6FDA–DABA–6FDA units in a large excess of 6FDA. These trimeric units were connected by adding the more reactive second diamine (*m*PD) to the reaction solution. Thereby, a statistical distribution of carboxylic acid groups, on

the average one carboxylic acid group in every tenth polymer unit is obtained in the copolyimide. With this method the ultimate crosslinking degree can be easily controlled by the stoichiometric ratio of diamines used in the polymerization reaction. Crosslinked copolyimides can be obtained by the treatment of crosslinkable copolyimides with ethylene glycol in DMAc, which is described later as “conventional crosslinking” method.

3.5. Membrane formation

All non-crosslinked polyimides and copolyimides showed good solubility in methylene chloride. For the

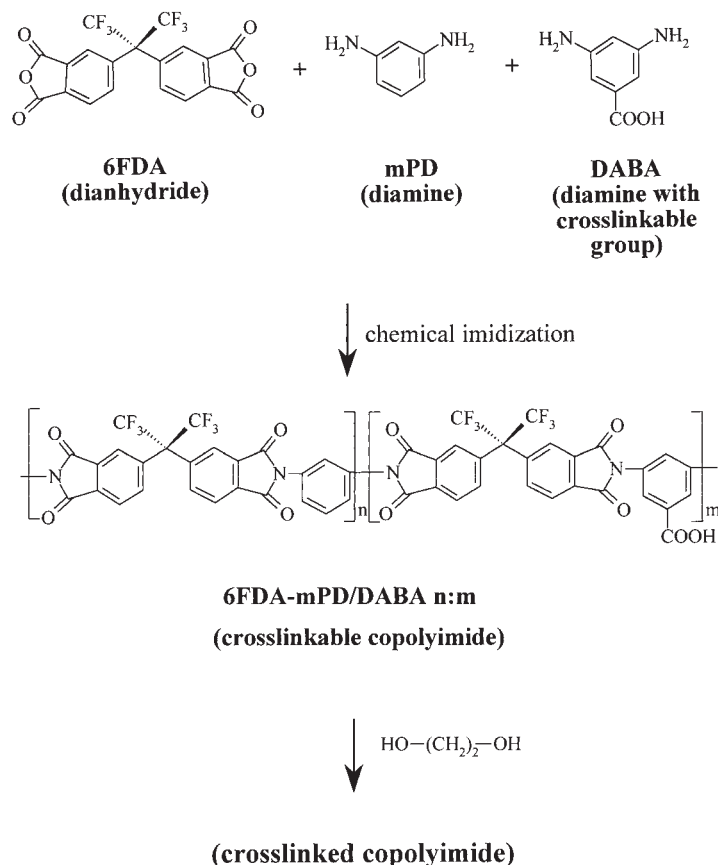


Fig. 2. Reaction scheme of the synthesis of crosslinked copolyimides.

preparation of membrane samples, the polymers were dissolved in methylene chloride and the solutions were filtered with 1 μm size filters to remove foreign particles which could induce defects in the film. For free film membrane samples, a 3–5 wt% polymer solution was used. After 4–8 h drying at room temperature, the films were removed with water from the glass plate. Composite membranes were prepared by casting a filtered 0.4–0.5 wt% polyimide/methylene chloride solution onto a porous anopore[®] disc (Whatman). All membrane samples were dried 14 h at 523 K under high vacuum to ensure that no residual solvent remains in the films.

3.6. Equipment and procedure

Steady-state gas permeabilities were determined at 308 K up to a feed pressure of 41 atm for CO₂ and CH₄

as well as for a 50:50 CO₂/CH₄ feed mixture using an apparatus described previously [13]. The equipment allows measurements of gas permeation rates by detection of the rate of accumulation of penetrants in the evacuated downstream receiver using an accurate pressure transducer. For mixed gas experiments, feed and permeate gas samples were analyzed by gas chromatography. The selectivity was calculated as described in Eq. (4).

4. Results and discussion

4.1. Pure gas permeation experiments

Table 2 shows the zeolite sieving diameter for CO₂, CH₄, O₂ and N₂ [14]. Table 3 shows the pure gas permeabilities and ideal CO₂/CH₄ and O₂/N₂ selectiv-

Table 2

Zeolite sieving diameter for the permeating penetrants in CO₂/CH₄ and O₂/N₂ separation [14]

Permeating penetrant	Zeolite sieving diameter (Å)
CO ₂	3.30
O ₂	3.46
N ₂	3.64
CH ₄	3.80

ities for the reference substance 6FDA-*m*PD, the crosslinked and uncrosslinked 6FDA-*m*PD/DABA 9:1 and the crosslinked 6FDA-DABA at 3.74 atm and 308 K. For the 6FDA-*m*PD polyimide used here as a reference substance, ideal CO₂/CH₄ selectivity calculated from pure gas permeability measurements at 308 K and 3.74 atm feed pressure is 58 with a CO₂ permeability of 11.03 Barrer, which is in good agreement with the data from Smit [15] and Tanaka et al. [16]. Generally, a strongly reduced permeability was found for the 6FDA-*m*PD/DABA 9:1 copolyimide containing a carboxylic acid group in every tenth polymer unit, compared to the reference substance 6FDA-*m*PD. Presumably the restricted chain mobility, reflected in the higher T_g compared to the 6FDA-*m*PD sample in Table 1, due to the hydrogen bonding between the free carboxylic acid groups, explains this difference. The reduction of the permeability is dependent on the molecular size of the permeation penetrant. Whereas, for small penetrants like CO₂ and O₂, 35–40% reduced permeability was found, for the larger N₂ and CH₄ a 37–47% reduced permeability was obtained for the 6FDA-*m*PD/DABA 9:1 copolyimide compared to the reference substance 6FDA-*m*PD. The result is an improved ideal selectivity for the 6FDA-*m*PD/DABA 9:1 of 65.3 compared to 58 with the 6FDA-*m*PD.

By crosslinking the 6FDA-*m*PD/DABA 9:1 copolyimide with ethylene glycol, “additional space” between the polymer chains is introduced, which means an increase in molecular free volume. As shown in Fig. 3 in the uncrosslinked 9:1 copolyimides the polymer chains are very close to each other. A three-dimensional very rigid structure is formed by hydrogen bonding. Actually, there are two hydrogen bondings on every carboxylic acid group and this is presumably the reason for the “tightening” of the molecular free volume and the strong reduction of permeability observed. Compared to the uncrosslinked 9:1 copolyimide, the crosslinked copolyimide shows a structure reflecting not only caused by creating additional space between the polymer chains due to insertion of ethylene glycol, but also by reducing the ultimate degree in crosslinking to a single crosslink per carboxylic acid group. Therefore, the CO₂ permeability of the chemical crosslinked copolyimide 6FDA-*m*PD/DABA 9:1 is 45% higher than with the uncrosslinked 9:1 copolyimide and somewhat lower than for the reference substance 6FDA-*m*PD. For the ideal CO₂/CH₄ and O₂/N₂ selectivity, no significant difference between the “pseudo-crosslinked” and the “chemical crosslinked” 9:1 copolyimide was observed. For high pressure CO₂ feeds, however, the advantages of chemical crosslinking will be shown to be clear.

For the crosslinked 6FDA-DABA, a very rigid polymer structure with a crosslink in every polyimide unit was obtained. For the crosslinked 6FDA-DABA, a slightly improved permeability for the small and medium sized gases CO₂, O₂ and N₂ was seen, with reduced permeability for the larger molecule CH₄ compared to the 10% crosslinked 6FDA-*m*PD/DABA 9:1. The higher CO₂, O₂ and N₂ permeabilities for the strongly crosslinked 6FDA-DABA were unexpected, and presumably primarily reflect an altered distribu-

Table 3

Pure gas permeabilities and ideal selectivities for the CO₂/CH₄ and O₂/N₂ separation at 3.74 atm and 308 K for 6FDA-*m*PD, 6FDA-*m*PD/DABA 9:1 non-crosslinked and crosslinked and 6FDA-DABA crosslinked

Polyimides	P_{CO_2} (Barrer)	P_{CH_4} (Barrer)	$\alpha_{\text{ideal}} (\text{CO}_2/\text{CH}_4)$	P_{O_2} (Barrer)	P_{N_2} (Barrer)	$\alpha_{\text{ideal}} (\text{O}_2/\text{N}_2)$
6FDA- <i>m</i> PD	11.03	0.19	58.0	2.60	0.40	6.5
6FDA- <i>m</i> PD/DABA 9:1	6.53	0.10	65.3	1.71	0.25	6.9
6FDA- <i>m</i> PD/DABA 9:1 (crosslinked)	9.50	0.15	63.3	1.81	0.27	6.8
6FDA-DABA (crosslinked)	10.40	0.12	87.0	2.69	0.40	6.7

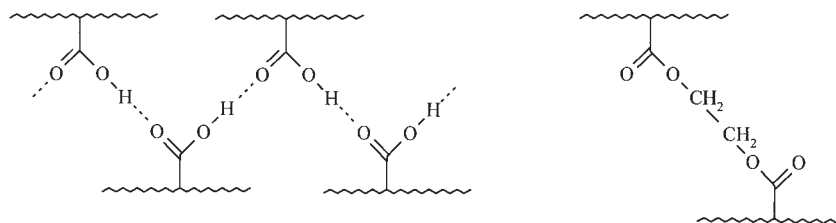


Fig. 3. Physical crosslinking effect due to hydrogen bonding between free carboxylic acid groups (left side) and chemical crosslinking by treatment of the free carboxylic acid groups with ethylene glycol (right side).

tion of fractional free volume within the material to favor permeation of smaller molecules. Complex solubility differences due to introduction of the glycol crosslinking agent to form ester links could also be a factor for the CO_2/CH_4 system. However, solubility data are not available to consider this effect. In any case, the spherocylindrically shaped CO_2 , O_2 and N_2 molecules are less well-characterized by a single dimension than is the essentially spherical CH_4 molecule. For instance, the effective dimensions of O_2 are 2.68 Å width and 3.75 Å length, which is characterized by the 3.46 Å “effective” diameter. On the other hand, CH_4 is well-characterized by the 3.8 Å diameter from all perspectives. In this connection CO_2 , O_2 and N_2 may be more able to access small transient gaps while CH_4 has less ability to access a fraction of the distribution of transient gaps constantly occurring in the crosslinked matrix. The ideal CO_2/CH_4 selectivity is 87 for the strong crosslinked 6FDA–DABA. The ideal O_2/N_2 selectivity is not influenced significantly by the degree of crosslinking because of the small difference in molecular size. Unusual high ideal H_2/CH_4 selectivity of 430 was already reported for the crosslinked 6FDA–DABA [17,18]. This latter result suggests that the principal change in the fractional free volume distribution is the introduction of more small volume elements, rather than a simple upward shifting of the total amount of free volume.

4.2. Plasticization due to high CO_2 pressure

As shown in Fig. 4 the reference substance 6FDA–*m*PD appears to undergo plasticization at around 5 atm CO_2 feed pressure in pure gas permeation experiments at 308 K. The 6FDA–*m*PD/DABA 9:1 copolyimide plasticizes at a much higher CO_2 pressure of 14 atm presumably due to hydrogen bondings between the

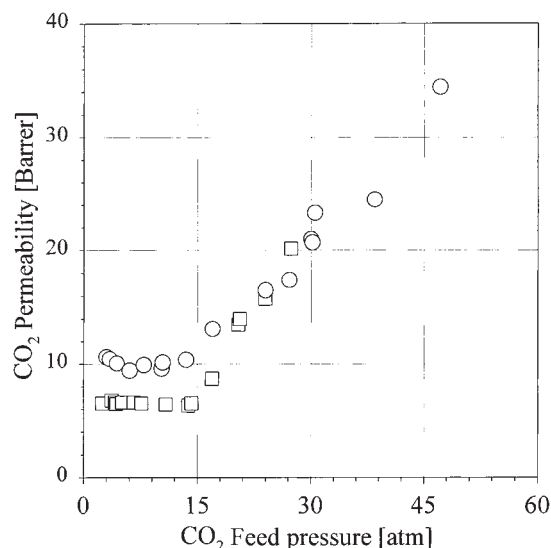


Fig. 4. Pure CO_2 permeability for the reference substance 6FDA–*m*PD (○) and the non-crosslinked 6FDA–*m*PD 9:1 copolyimide (□) at 308 K.

carboxylic acid groups. In the presence of a humid feed, these virtual crosslinks are likely to be compromised. As shown in Fig. 5 with the actual chemical crosslinked 6FDA–*m*PD/DABA 9:1 copolyimide no plasticization effect is observed at CO_2 pressure beyond 35 atm. The effects of humidity on this interesting material was not part of this study, but should be investigated from a practical standpoint, since moisture is often a component in natural gas feeds. A decreasing CO_2 permeability with increasing CO_2 pressure seen for these glassy materials is consistent with the well-known “dual mode sorption” and transport model predictions. The eventual upturn in CO_2 permeability is associated with swelling and plasticization of the matrix by CO_2 (Eq. (3)). The strongly

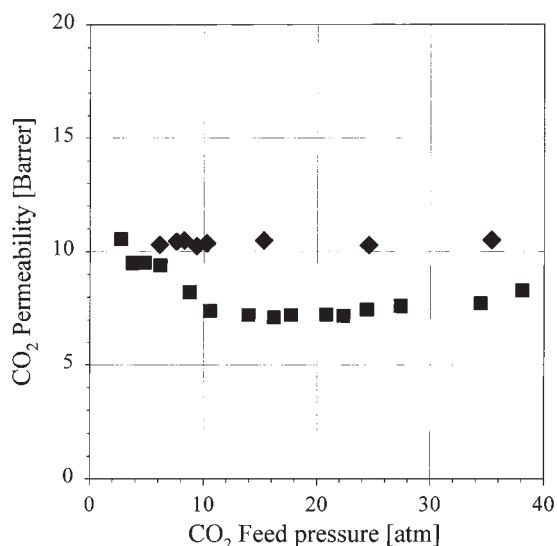


Fig. 5. Pure CO_2 permeability for the crosslinked 6FDA-*m*PD/DABA 9:1 copolyimide (■) and the crosslinked 6FDA-DABA (◆) at 308 K.

crosslinked 6FDA-DABA did not show any signs of plasticization up to a CO_2 feed pressure of 35 atm. Because of the high degree of crosslinking a very rigid polyimide structure was obtained. An almost constant CO_2 permeability was reached over the whole investigated CO_2 pressure range.

4.3. Mixed gas experiments

Mixed gas experiments with a 50:50 feed mixture at 308 K for total feed pressures up to 20 atm have been conducted for the 6FDA-*m*PD reference substance. The results for crosslinked and non-crosslinked 6FDA-*m*PD/DABA 9:1 and the crosslinked 6FDA-DABA are shown in Fig. 6.

With the uncrosslinked 6FDA-*m*PD reference polyimide, selectivity is around 40 at feed pressure of 10 atm and lower. At higher feed pressure, CO_2/CH_4 selectivity decreases rapidly because of CO_2 swelling and plasticization. As expected from pure gas permeation experiments, with the 6FDA-*m*PD/DABA 9:1 copolyimide, pseudo-crosslinked or chemically crosslinked, CO_2/CH_4 selectivity is constant at around 48 up to a total feed pressure of 25 atm. For a total feed pressure of over 28 atm in 50:50 mixed gas feeds (a

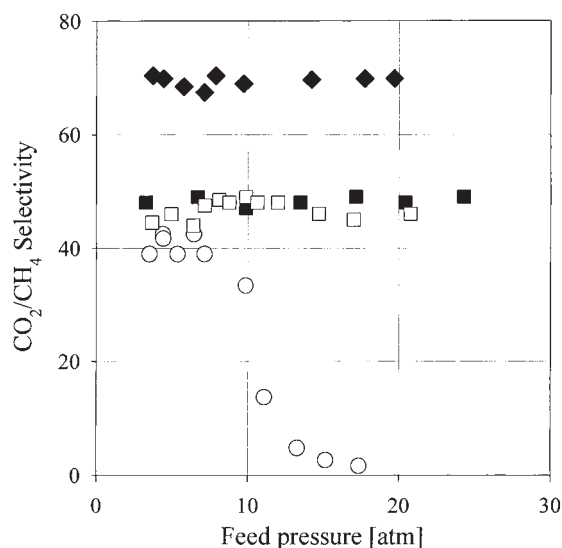


Fig. 6. CO_2/CH_4 selectivity in mixed gas experiment with a 50:50 CO_2/CH_4 feed mixture for the 6FDA-*m*PD (○), the non-crosslinked 6FDA-*m*PD/DABA 9:1 copolyimide (□), the crosslinked 6FDA-*m*PD/DABA 9:1 copolyimide (■) and the crosslinked 6FDA-DABA (◆) at 308 K.

partial CO_2 feed pressure of over 14 atm), for the uncrosslinked 6FDA-*m*PD/DABA 9:1 copolyimide, a loss in selectivity is also expected. For the strongly crosslinked 6FDA-DABA polyimide, a very high CO_2/CH_4 selectivity of 70 is obtained in mixed gas experiments and plasticization and swelling-induced permselectivity losses were not observed for the conditions studied here up to a total feed pressure of 20 atm.

4.4. Crosslinking as a post-treatment

As Fig. 7 shows, the “conventional” method of preparing crosslinked film samples involves casting a solution of copolyimide or polyimide containing free carboxylic acid groups in dimethyl acetamide and ethylene glycol on a heated teflon plate. For crosslinking, the obtained films were heated to 523 K for 24 h.

A second method of crosslinking was investigated, because it would be difficult to spin hollow fibers from DMAc in the presence of the crosslinking agent ethylene glycol. Moreover, the practical drying temperature should not exceed 403–423 K, to allow use in a composite form with common support layers such as

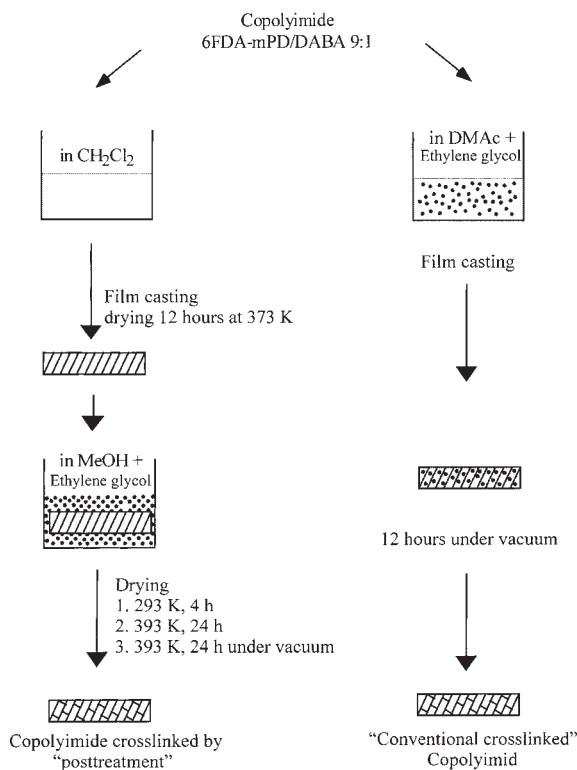


Fig. 7. Different methods of crosslinking: “conventional crosslinking” on the right side and crosslinking as a “post-treatment” on the left side.

UDE[®] or ULTEM[®] which have softening temperatures of 453 and 503 K, respectively. The possibility of crosslinking as a “post-treatment” as shown in Fig. 7 was investigated with free film samples. For the method of crosslinking as a post-treatment, a crosslinkable copolyimide was cast from a methylene chloride solution. The obtained films, still containing free carboxylic acid groups were dried 12 h at 373 K. The film samples were immersed in a 80:20 methanol–glycol solution. Methanol was used for swelling the polymer structure. After 8 h the samples were taken out of the solution and dried 4 h at room temperature (evaporation of methanol), 12 h at 393 K (for the crosslinking reaction) and finally 24 h under vacuum at 393 K (to remove the still remaining ethylene glycol). H_2 , CO_2 and CH_4 permeability measurements are in good agreement for “conventional” crosslinked films and for the film samples obtained with the “post-treatment” as shown in Table 4. Clearly, the effects of the ethylene glycol and elevated temperature exposure

Table 4

Pure gas permeabilities of different crosslinked 6FDA-mPD/DABA 9:1 membrane samples at 3.74 atm feed pressure and 308 K

Crosslinking method	P_{H_2} (Barrer)	P_{CO_2} (Barrer)	P_{CO_2} (Barrer)
Conventional crosslinking	38.20	9.50	0.15
Crosslinking as a posttreatment	38.60	9.80	0.15

on asymmetric support layers used in composite applications should be investigated, but this was outside the scope of the present work. It is anticipated that some morphological changes in support layers may result, but that can probably be adjusted in the formation process used to make the support layer. Besides composite membranes for gas separation, these crosslinked materials could be useful as a simple monolithic asymmetric membrane to achieve a high degree of resistance to swelling and plasticization by regular stream components and contaminants. Pervaporation applications typify such cases.

5. Conclusion

Incorporation of polar groups ($-\text{COOH}$) in polyimide structures leads to a strongly reduced permeability. Plasticization due to CO_2 can be reduced, but not eliminated in the presence of such “virtual” hydrogen bonded crosslinks.

By true chemical crosslinking of $-\text{COOH}$ groups with ethylene glycol polyimides or copolyimides were formed that showed no plasticization up to 35 atm pure CO_2 pressure. Even with a 10% degree of crosslinking, a 20% increased selectivity was seen compared to the reference polyimide. Because of additional space between the polymer chains, which means an increase in molecular free volume, caused by the crosslinking agent, only small loss in permeability was found for the crosslinked copolyimides, compared with the non-crosslinked reference polyimide.

Fig. 8 shows the “trade off” for the CO_2/CH_4 separation [19]. For the crosslinked and the uncrosslinked 6FDA-mPD/DABA 9:1 copolyimide separation properties nearby other “upper bond” polyimides are obtained. On the other hand, the CO_2/CH_4 separation properties of the strong crosslinked 6FDA-DABA are much better with an ideal selectivity of 87 and a

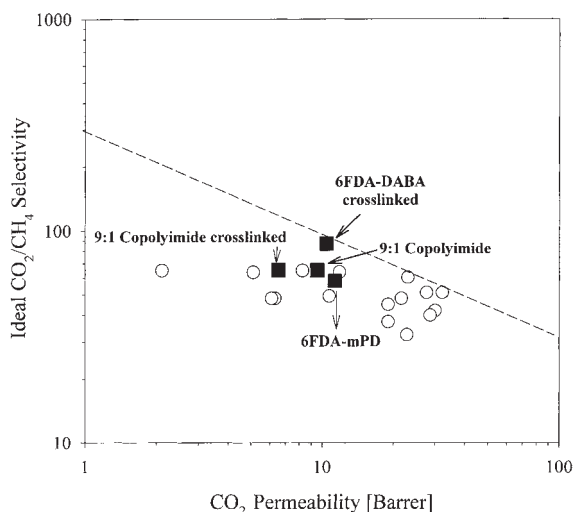


Fig. 8. "Trade off" for the CO_2/CH_4 separation, (○) 6FDA-based polyimides [16], (■) polyimides synthesized in this study. The dashed line represents the so-called "upper bond" of performance trade off reported by Robeson [19].

CO_2 permeability of 10.4 Barrer. By using the method of chemical crosslinking as described in this study, the CO_2/CH_2 separation characteristics of polyimides can be decisively improved without a significant loss in CO_2 permeability.

Crosslinking as a post-treatment with drying temperatures below 393 K was successful with different film samples. Posttreated film samples show the same permeabilities as film samples crosslinked by the conventional method. Further investigations will show if the method of post-treatment which was shown for free film membrane samples is applicable in hollow fiber preparation.

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