



NRC Publications Archive Archives des publications du CNRC

Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1)

Thomas, Sylvie; Pinnau, Ingo; Du, Naiying; Guiver, Michael D.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.memsci.2009.02.003>

Journal of Membrane Science, 333, May, pp. 125-131, 2009

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=607fd0ef-249d-4b74-b5f2-e956821e341f>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=607fd0ef-249d-4b74-b5f2-e956821e341f>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.





Pure- and mixed-gas permeation properties of a microporous spirobisindane-based ladder polymer (PIM-1)

Sylvie Thomas^a, Ingo Pinnau^{a,*}, Naiying Du^b, Michael D. Guiver^b

^a Membrane Technology and Research, Inc., 1360 Willow Road, Suite 103, Menlo Park, CA 94025, USA

^b Institute for Chemical Process and Environmental Technology, National Research Council of Canada, 1200 Montreal Road, Ottawa, ON, K1A 0R6, Canada

ARTICLE INFO

Article history:

Received 3 December 2008

Received in revised form 27 January 2009

Accepted 5 February 2009

Available online 13 February 2009

Keywords:

PIM

Microporosity

Ladder polymers

Gas permeation

Mixtures

Temperature

ABSTRACT

PIM-1, a glassy, spirobisindane-based ladder polymer is a novel intrinsically microporous membrane material. The pure- and mixed-gas permeation properties of PIM-1 are compared to those of highly permeable, microporous, linear chain, acetylene-based polymers, such as poly(1-trimethylsilyl-1-propyne) (PTMSP). PIM-1 exhibits very high permanent gas permeabilities coupled with moderate selectivities. For example, the oxygen permeability of PIM-1 at 25 °C is $1300 \times 10^{-10} \text{ cm}^3 \text{ (STP) cm/cm}^2 \text{ s cmHg}$ combined with an oxygen/nitrogen selectivity of 3.8. Those values place PIM-1 above the Robeson trade-off curve for oxygen/nitrogen separation. Like microporous linear chain PTMSP, ladder-type PIM-1 is more permeable to large, condensable organic vapors, such as *n*-butane, than to small, permanent gases, such as methane. PIM-1 exhibits a mixed-gas *n*-butane/methane selectivity of up to 25, which is similar to that of PTMSP, the most permeable and selective polymer known for this separation. Because PIM-1 has significantly better solvent resistance than PTMSP, it could find applications as an advanced membrane material for the separation of organic vapor/permanent gas mixtures.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

During the last three decades, membrane-based gas separation has become a well-established unit operation for a variety of important applications, such as nitrogen enrichment from air, hydrogen recovery from inert gases in the petrochemical industry, and carbon dioxide removal from natural gas [1–3]. In these applications, low-free-volume glassy polymer membranes, such as cellulose acetate, polysulfone or polyimides, are in commercial use. Recently, membrane processes have also been applied to the (i) removal of heavy hydrocarbons (C_{3+}) from methane to control the heating value and dew point of natural gas and (ii) recovery of hydrogen and/or hydrocarbons from petrochemical waste gas streams [3–6]. In most of these hydrocarbon–vapor-containing feed streams, the product gas (methane or hydrogen) is the major component. To minimize membrane area requirements (which lower capital cost) and to eliminate recompression by maintaining the product gas at feed pressure, it is highly desirable to use membranes that are solubility-selective for vapors of large hydrocarbons, instead of using size-sieving permanent-gas-selective membranes [6–8]. Existing commercial rubbery polydimethylsiloxane (PDMS) membranes show only moderate performance for these separa-

tions. The limited use of PDMS membranes arises mainly from their modest C_{3+} /methane and C_{3+} /hydrogen selectivities [5].

About 25 years ago, Masuda et al. [9–12] discovered poly(1-trimethylsilyl-1-propyne) (PTMSP), the first microporous glassy polymer ever reported. While PTMSP has the highest pure-gas permeability of any known polymer, the extremely high gas permeability is coupled with very low pure-gas selectivities. In this regard, we define polymers with average chain spacing of 7–20 Å as microporous materials. This classification falls within the general IUPAC definition of micropores in inorganic solids (pore size <20 Å) [13]. It is important to note that based on our definition, conventional low-free-volume, glassy polymers, such as polycarbonates and polysulfones, are *not* microporous materials because their average chain spacing is less than 7 Å based on wide-angle X-ray diffraction (WAXD) data [14,15]. On the other hand, some recently developed high-free-volume, glassy polymers, such as PTMSP [16] and some aromatic polyimides [17,18] have average chain spacing larger than 7 Å. In addition, these latter polymers have extraordinarily high BET surface area (>200 m²/g), which is typical for finely microporous media.

Because of its intrinsic microporous morphology, PTMSP exhibits unusual permeation properties for large condensable gases, such as C_{3+} hydrocarbons and other organic vapors. Contrary to the permeation behavior of conventional low-free-volume glassy polymers, PTMSP is significantly more permeable to large organic vapors than to small, permanent gases. In fact, in the separation

* Corresponding author. Tel.: +1 650 328 2228x113; fax: +1 650 328 6580.
E-mail address: ipin@mtrinc.com (I. Pinnau).

of heavy hydrocarbons from methane or hydrogen, PTMSP exhibits the highest mixed-gas C_{3+} permeability coupled with the highest C_{3+} /methane and C_{3+} /hydrogen selectivity of all known polymers [19–22].

Microporous high-free-volume glassy polymers like PTMSP are characterized by [19–24]: (i) high-free-volume (>20% of the total volume of polymer), (ii) large inter- and intrachain spacing (~5–20 Å), (iii) connectivity of free volume elements, (iv) very high BET surface area (~200–800 m²/g), (v) high pure- and mixed-gas permeability and high vapor/permanent-gas mixture selectivity, (vi) blocking (reduction in permeability) of permanent gases by co-permeation of condensable components in the feed mixture, and (vii) negative or very slightly positive activation energy of gas permeation. All of these properties are commonly observed in inorganic microporous (pore size <20 Å) materials, such as glass or carbon membranes [25,26], but are typically not observed in conventional, low-free-volume glassy polymers.

Because of its outstanding mixed-gas separation properties, PTMSP was previously considered to be a promising membrane material for C_{3+} /methane and C_{3+} /hydrogen separation. However, PTMSP is soluble in liquid hydrocarbons, and therefore cannot be used in these industrial applications [27,28]. Hence, novel microporous glassy polymers with the exceptional mixed-gas permeation properties of PTMSP and significantly better solvent resistance are required as advanced membrane materials for separations involving condensable hydrocarbons.

A new class of microporous glassy polymers was recently introduced by Budd, McKeown et al. [29–36]. These materials are rigid, highly contorted spirobisindane-based ladder polymers, and have essentially no rotational freedom in the polymer backbone, resulting in large free volume as indicated by BET surface areas of ~800 m²/g [36]. PIM-1, the first reported high molecular weight microporous ladder polymer in this class, exhibits very high permanent gas permeabilities, similar to those of microporous, acetylene-based polymers [30]. In this paper, the mixed-gas permeation properties of PIM-1 are reported for the first time for *n*-butane/methane mixtures and compared with those of microporous PTMSP. In addition, the effects of temperature and film formation protocols on the pure-gas permeation properties of PIM-1 are discussed.

2. Experimental

2.1. Polymer synthesis

PIM-1 was synthesized using a recently developed high-intensity mixing polycondensation reaction described by Du et al. [37]. The monomer 3,3,3',3'-tetramethyl-1,1'-spirobisindane-5,5',6,6'-tetrol (TTSBI, 98%) was obtained from Alfa Aesar and purified by recrystallization from an ethanol–dichloromethane solvent mixture. The second monomer – 2,3,5,6-tetrafluorophthalonitrile (DCTB) – was purchased from Matrix Scientific and purified by vacuum sublimation at 140–150 °C. All glassware was oven-dried prior to the polycondensation to ensure completely anhydrous conditions. A flask was charged with 5.106 g (15 mmol) of TTSBI, 3.003 g (15 mmol) of DCTB, 6.2 g (45 mmol) K₂CO₃, and 25 mL DMAc. Under an argon environment and at a temperature of 155 °C, the mixture was vigorously stirred with a high-intensity mixer for 2 min and then 20 mL toluene was added to the reaction mixture. The reaction was continued for 2 min, when precipitate appeared and the reaction mixture became viscous. Another 20 mL toluene was added; otherwise, mixing could not be continued easily. After two more minutes, the polymer was isolated by precipitation with methanol and filtered. Following re-precipitation with a chloroform/methanol mixture, the polymer was boiled in hot water for several hours to remove the salt and solvent, then filtered off

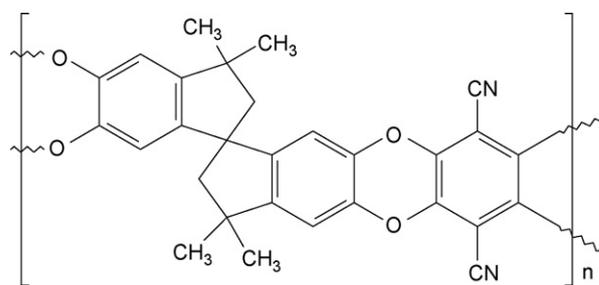


Fig. 1. Repeat unit of PIM-1.

and dried overnight at 60 °C under vacuum to give 91% yield. The molecular weight, determined by gel chromatography, was $M_n = 101,000$ g/mol and $M_w = 257,000$ g/mol. The structure of PIM-1 is shown in Fig. 1.

2.2. Polymer film preparation

Isotropic films of PIM-1 were prepared by slowly pouring a filtered 2 wt% chloroform solution of the polymer into a flat-bottomed glass Petri dish, which was then covered with a glass plate to slow down solvent evaporation. The films were initially dried at ambient temperature for two days, then removed from the glass dish and placed in a vacuum oven at 70 °C to remove any residual solvent. Thereafter, the films were immersed in methanol for 2 h at ambient conditions to reverse prior film formation history, in a manner similar to protocols previously developed for microporous polyacetylenes and PIM-1 [38–40]. After removal from methanol, the films were dried gradually at 70 °C in air, and weighed intermittently until constant weight was obtained. Preconditioning ensures preparation of PIM-1 samples with reasonably reproducible permeation properties (± 10 –20%).

2.3. Film characterization

The thicknesses of the PIM-1 films tested in this study ranged between 50 and 80 μm and were determined with a digital micrometer readable to ± 1 μm . The films were bright yellow, transparent and mechanically strong. The samples were weighed on an analytical balance and their densities were calculated, using the known sample area and thickness. The densities ranged from 1.07 to 1.09 g/cm³, essentially identical to values previously reported by Budd et al. [35]. The fractional free volume (*FFV*) (cm³ of free volume/cm³ polymer) commonly used as a measure for the free volume available for chain packing, can be determined from

$$FFV = \frac{v_{sp} - 1.3v_w}{v_{sp}} \quad (1)$$

where v_{sp} is the specific volume (cm³/g) of the polymer, as determined from density measurements. The van der Waals volume, v_w , estimated from van Krevelen's group contribution method, was 0.54 g/cm³ [41]. Some of the volumetric physical properties of PIM-1 are compared to those of PTMSP in Table 1. Based on the measured densities of several isotropic PIM-1 films, the polymer's *FFV* ranged from 0.24 to 0.26 cm³ free volume/cm³ polymer. The *FFV* of PIM-1

Table 1
Volumetric physical properties of PIM-1 and PTMSP.

Polymer	PIM-1	PTMSP
BET surface area (m ² /g)	760 [36] 830 [37]	780 [24]
PALS chain spacing (Å)	5.8–10.6 [43]	5.1–12.4 [43]
Fractional free volume (%)	24–26	29 [24]

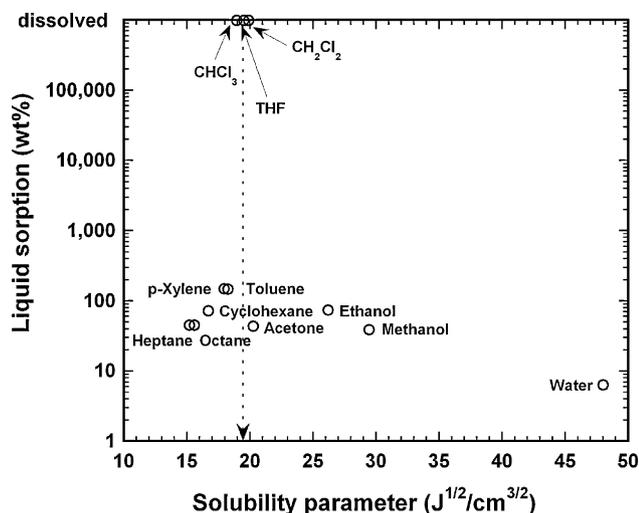


Fig. 2. Sorption of organic liquids and water in PIM-1 as function of solvent solubility parameter.

is higher than that of conventional glassy polymers, which is typically in the range of 0.16–0.22, but lower than the FFV value of microporous PTMSP [24]. PTMSP and PIM-1 have high BET surface areas of 780 and 760 m²/g, respectively [24,29]. These values are very similar to those of microporous inorganic materials such as carbons, clearly indicating that the polymers have intrinsic microporosity. Based on positron annihilation lifetime spectroscopy (PALS) studies, both PIM-1 and PTMSP have a bimodal pore size distribution [42,43]. Both polymers have chain (pore) spacings of about 5–12 Å [43]. However, it is noteworthy that PTMSP has a much larger fraction of wider pores than PIM-1, a difference that has a significant impact on the gas and vapor permeation properties of these polymers [43].

2.4. Solubility and swelling of solvents in PIM-1

To determine the solvent resistance of PIM-1, film samples of known weight were immersed in various solvents at 25 °C in small glass vials until equilibrium mass uptake was obtained, which typically occurred within two days. After carefully removing the excess solvent from the film surfaces, the weight increase was measured immediately, using an analytical balance. PIM-1 swells significantly in most solvents, as shown in Fig. 2. For example, PIM-1 sorbs about 45 wt% *n*-heptane and 150 wt% toluene at 25 °C. On the other hand, PIM-1 is soluble in only a few solvents. Among the 12 solvents tested, PIM-1 is soluble only in chloroform, dichloromethane, and tetrahydrofuran. The solubility parameter of PIM-1, based on swelling measurements, is 19.5 J^{1/2}/cm^{3/2}.

2.5. Gas permeation measurements

2.5.1. Pure-gas permeation measurements

The pure-gas permeation properties of a PIM-1 film were determined using the constant pressure/variable volume method. The permeation experiments were carried out at a feed pressure of 65 psi (except for *n*-butane: $p_{\text{feed}} = 30$ psi); the permeate pressure was atmospheric (15 psi). The order of gas permeation measurements was nitrogen, methane, oxygen, helium, hydrogen, carbon dioxide, ethane, propane, and *n*-butane. The feed and permeate side of the permeation cell were always purged with the test gas prior to any gas permeation measurement. The experimental temperature was varied between 0 and 55 °C. The permeate flow rate was measured using a soap-bubble flow meter supplied by Alltech (Colombia, MD).

The steady-state flux, J , determined by the constant pressure/variable volume method, is calculated from

$$J = \frac{273.15 p_a}{76 T A} \left(\frac{dV}{dt} \right) \quad (2)$$

where J is the steady-state gas flux (cm³(STP)/cm² s), A is the membrane area (cm²), p_a is the atmospheric pressure (cmHg), T is the gas temperature (K) and dV/dt is the volumetric displacement rate of the soap film in the bubble flow meter (cm³/s). The gas permeability coefficient P (cm³ (STP) cm/cm² s cmHg) was determined using the relationship:

$$P = \frac{Jl}{(p_2 - p_1)} \quad (3)$$

where l is the membrane film thickness (cm), and p_2 and p_1 are the feed and the permeate pressure (cmHg), respectively.

The pure-gas selectivity, α , is defined as the ratio of the permeability coefficients of gases A and B:

$$\alpha_{AB} = \frac{P_A}{P_B} \quad (4)$$

2.5.2. Mixed-gas permeation measurements

Mixed-gas permeation measurements were carried out with *n*-butane/methane mixtures, the separation of which is important for control of hydrocarbon content in natural gas. The *n*-butane concentration in the feed mixture was varied between 0.5 and 7.4 vol.%. The experiments were performed at 25 °C at a feed pressure of 150 psig; the permeate pressure was atmospheric (0 psig). The residue and permeate compositions were determined using a gas chromatograph equipped with a thermal conductivity detector (TCD). The stage cut, that is, the ratio of permeate to feed flow rate, was always kept below 1%. Under these conditions, the residue composition is essentially equal to the feed composition. The mixed-gas permeability coefficients were calculated using:

$$P = \frac{x_{\text{perm}} J_{\text{perm}} l}{(p_{\text{feed}} x_{\text{feed}}) - (p_{\text{perm}} x_{\text{perm}})} \quad (5)$$

where x_{perm} and x_{feed} are the mole fractions of the gas components in the permeate and feed stream, respectively; J_{perm} is the total permeate flux (cm³/cm² s); l is the film thickness; and p_{perm} and p_{feed} are the absolute permeate and feed pressures (cmHg), respectively. The gas mixture selectivity was determined using Eq. (4).

3. Results and discussion

3.1. Pure-gas permeation properties of PIM-1

The pure-gas permeabilities of PIM-1 and PTMSP, two microporous, high-free-volume, glassy polymers, and polysulfone, a conventional glassy polymer, are shown in Fig. 3, as a function of the Lennard–Jones gas diameters. The gas permeabilities in polysulfone decrease significantly as the penetrant size increases. In conventional glassy polymers, gas size has a much larger effect on diffusion than on solubility, which leads to a dramatic decrease in permeability as the size of the gas molecules increases. On the other hand, as a general trend, the permeabilities of PTMSP and PIM-1 increase as the molecular size of the gases increases; this behavior is unusual for conventional glassy polymers, but consistent with that of microporous inorganic materials with pore dimensions of less than 20 Å. In microporous glassy polymers, the diffusion coefficients show only a relatively weak dependence on gas size and, hence, gas transport is often more influenced by gas solubility [7] than diffusion. PIM-1 gas permeability coefficients are lower than those of PTMSP because PIM-1 has lower FFV and smaller average chain (pore) spacing compared to PTMSP, based on previously reported PALS data [43].

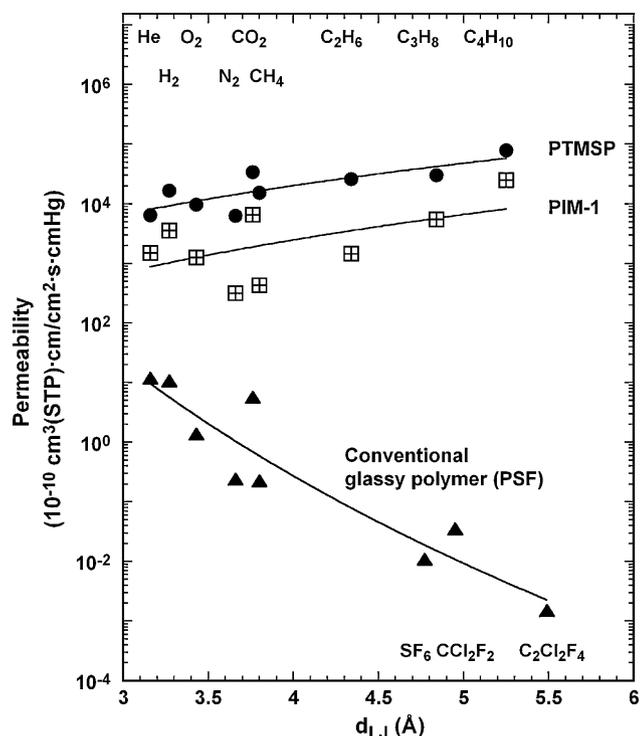


Fig. 3. Pure-gas permeabilities of microporous PIM-1 and PTMSP, and low-free-volume polysulfone as function of Lennard-Jones gas diameter. $T = 23\text{--}25\text{ }^{\circ}\text{C}$.

The permeation properties of PIM-1 are summarized in Table 2 for various gases, in terms of permeability coefficients and selectivity over nitrogen. PIM-1 exhibits very high permeabilities coupled with moderate selectivity. For example, the oxygen permeability coefficient in our study is about 1300 Barrer ($10^{-10}\text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{ s cmHg}$) with an oxygen/nitrogen selectivity of 3.8. Those values place PIM-1 above the Robeson trade-off curve for oxygen/nitrogen separation [44,45]. Ladder-type PIM-1 exhibits much higher selectivity for permanent gases, such as oxygen and nitrogen, than microporous acetylene-based polymers. For example, PTMSP has an oxygen/nitrogen selectivity of only 1.4. Most likely, the higher oxygen/nitrogen selectivity of PIM-1 results from smaller, more size-sieving free volume elements.

It is interesting to note that the permeability and selectivity values for PIM-1 can vary significantly [30,40,46,47]. For example, our permeability values are significantly higher than those reported by Budd et al. [30], whereas gas selectivities are lower. It is well known that the permeability of highly rigid glassy polymers can vary significantly depending on the film formation protocols [48].

Table 2

Pure-gas permeability and selectivity of PIM-1. This study: feed pressure: 65 psi; permeate pressure: 15 psi; $T = 25\text{ }^{\circ}\text{C}$. Budd et al. [30]: feed pressure: 4.5 psi; permeate pressure: ~ 0 psi; $T = 30\text{ }^{\circ}\text{C}$. Staiger et al. [43]: feed pressure: 59 psi; permeate pressure: ~ 0 psi; $T = 35\text{ }^{\circ}\text{C}$.

Gas	Permeability (Barrer ^a)			Selectivity (gas/N ₂)		
	This work	Staiger	Budd	This work	Staiger	Budd
N ₂	340	238	92	–	–	–
CH ₄	430	360	125	1.3	1.5	1.4
O ₂	1,300	786	370	3.8	3.3	4.0
He	1,500	1061	660	4.4	4.5	7.2
H ₂	3,600	2332	1300	11	10	14
CO ₂	6,500	3496	2300	19	15	25
C ₂ H ₆	1,500	–	–	4.4	–	–
C ₃ H ₈	5,500	–	–	16	–	–
<i>n</i> -C ₄ H ₁₀	25,100	–	–	74	–	–

^a 1 Barrer = $10^{-10}\text{ cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{ s cmHg}$.

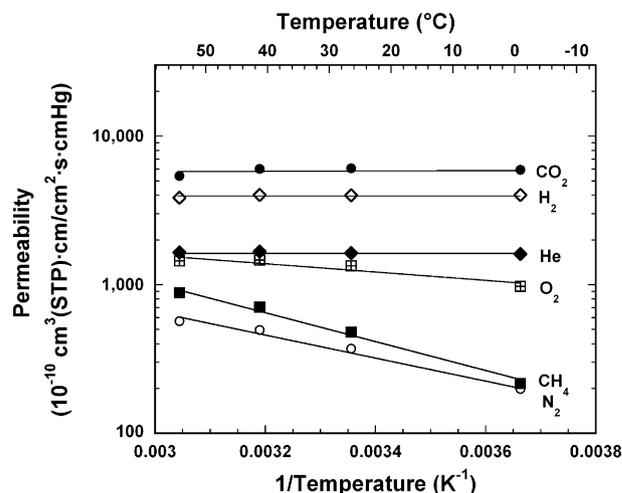


Fig. 4. Permeability of PIM-1 for various gases as function of reciprocal temperature. Feed pressure: 50 psig; permeate pressure: atmospheric (0 psig).

For example, solvent type and drying conditions can influence polymer chain packing, which, in turn, affects gas permeability and selectivity. As described above, our films were made from chloroform solution, dried in an oven at $70\text{ }^{\circ}\text{C}$, methanol-conditioned and finally dried again at $70\text{ }^{\circ}\text{C}$ in air. The permeability data reported by Budd et al. were measured using a PIM-1 film made from tetrahydrofuran and dried at ambient temperature with a nitrogen purge. It is suggested that these differences in PIM-1 film formation caused the differences in gas permeability and selectivity. Recent data reported by Staiger et al. [43] support our hypothesis; the pure-gas permeabilities and selectivities of a PIM-1 film made from methylene chloride are similar to our data for a chloroform solution-cast PIM-1 film. Current work is directed at investigating the effects of solvent type and drying conditions on the permeability and selectivity of microporous PIM-1 in more detail. We will report the results in a future publication.

3.2. Effect of temperature on pure-gas permeability of PIM-1

Gas permeabilities of PIM-1 determined at temperatures ranging from 0 to $55\text{ }^{\circ}\text{C}$ are shown in Fig. 4. The temperature dependence of gas permeability in polymers is given by the Arrhenius relationship:

$$P = P_0 \exp\left(-\frac{E_p}{RT}\right) \quad (6)$$

where P_0 is a pre-exponential factor ($\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{ s cmHg}$), E_p is the activation energy of permeation (J/mol), T is the temperature (K) and R is the ideal gas constant ($8.314\text{ J}/\text{mol K}$). E_p values for PIM-1 were determined from the slopes ($-E_p/R$) of the best curve-fits through the permeation data in Fig. 4. The E_p values are summarized in Table 3. Methane and nitrogen permeability of PIM-1 depend strongly on temperature and their E_p values are essentially of the

Table 3

Activation energy of permeation (E_p) for PIM-1, PTMSP and polycarbonate.

Gas	E_p (J/mol)		
	PIM-1 (this study)	PTMSP [50]	Polycarbonate [51]
CH ₄	19,400	–5,300	25,960
N ₂	14,300	–3,500	23,000
O ₂	5,600	–5,500	20,940
He	400	500	17,570
H ₂	–400	–2,100	–
CO ₂	–1,000	–11,700	12,550

Table 4

Mixed-gas permeation properties of microporous, glassy PIM-1, PTMSP, and rubbery PDMS [52]. Feed: 2 vol.% *n*-butane in methane; feed pressure: 150 psig; permeate pressure: 0 psig; temperature: 25 °C.

Material	Permeability coefficient $\times 10^{10}$ ($\text{cm}^3(\text{STP})\text{cm}/\text{cm}^2\text{s cmHg}$)		Selectivity $n\text{-C}_4\text{H}_{10}/\text{CH}_4$	Mixed-gas/pure-gas CH_4 permeability ratio
	$n\text{-C}_4\text{H}_{10}$	CH_4		
PIM-1	4,200	175	24	0.7
PTMSP [19]	53,500	1,800	30	0.1
PDMS [52]	12,900	1,250	10	1.2

same order of magnitude as those of conventional glassy polymers, such as bisphenol-A polycarbonate. For the smaller gases – helium, hydrogen, oxygen, and carbon dioxide – the dependence of permeability on temperature is much weaker; hence, the E_p values are significantly lower than those of low-free-volume glassy polymers. PIM-1 has much higher activation energies of permeation than PTMSP, except with helium. This result suggests that diffusion through microporous polymers with similar BET surface area values can differ significantly because of differences in the average free volume element size and connectivity of the microporous structure.

3.3. Mixed-gas permeation properties of PIM-1

It was previously demonstrated that PTMSP has unusual organic vapor/permanent mixed-gas permeation properties [19–22]. PTMSP is more permeable to large condensable hydrocarbons than to small permanent gases such as methane, nitrogen or hydrogen. It was shown that PTMSP has a mixed-gas *n*-butane/methane selectivity of about 30 for a mixture containing 2 vol.% *n*-butane in methane, which is six times higher than its pure-gas *n*-butane/methane selectivity. The mixed-gas permeation properties of PIM-1 are presented in Table 4; the mixed-gas behavior of PIM-1 is qualitatively similar to that of PTMSP. For a gas mixture containing 2 vol.% *n*-butane in methane at a feed pressure of 150 psig and at 25 °C, PIM-1 has an *n*-butane permeability of 4200 Barrer and *n*-butane/methane selectivity of 24. This result indicates that the *n*-butane/methane selectivity of PIM-1 is dominated by high solubility selectivity and low diffusivity selectivity, similar to that of PTMSP [22]. Like PTMSP, PIM-1 has unusual permeation properties due its high excess free volume, large chain spacing, and interconnectivity of free volume elements. However, the *n*-butane mixed-gas permeability of PIM-1 is about 13-fold lower than that of PTMSP; this probably results from its lower free volume, smaller average chain spacing in the polymer matrix, and smaller fraction of large free volume elements. Another difference between the mixed-gas permeation properties of PIM-1 and PTMSP is the reduction in methane permeability in mixtures with *n*-butane, relative to their pure-gas methane permeabilities. The blocking effect of methane by co-permeation of the significantly more condensable and larger *n*-butane is a typical characteristic of microporous polymers, such as PTMSP [19–23]. When tested under the same experimental conditions, the mixed-gas methane permeabilities of PIM-1 and PTMSP are reduced to 70% and 10% of their pure-gas methane permeability, respectively. This result indicates that PTMSP has larger average free volume elements than PIM-1, which are blocked more efficiently by co-permeation of *n*-butane in mixture experiments.

The gas permeation properties of *n*-butane/methane mixtures in PIM-1 are very time-dependent. The long-term permeation results for a 2 vol.%/98 vol.% *n*-butane/methane mixture are shown in Fig. 5a and b. The initial 30-min *n*-butane permeability increased 4-fold from 975 Barrer to the steady-state value of about 4300 Barrer after 24 h. On the other hand, the methane permeability of 180 Barrer was essentially constant over the same time interval. Consequently, the *n*-butane/methane selectivity increased from 5.6 to 24 over a period of 24 h. It appears that, due to significant sorption, *n*-butane dilates the polymer matrix, increasing the size of

the free volume elements. Because of the dilated, more open polymer matrix, the *n*-butane diffusion coefficient increases, which leads to an increase in *n*-butane permeability. This behavior is in stark contrast to that of microporous PTMSP, in which steady-state mixed-gas permeation properties are attained over short time scales (<1 h). We suggest that differences in free volume element size and distribution between PIM-1 and PTMSP are responsible for

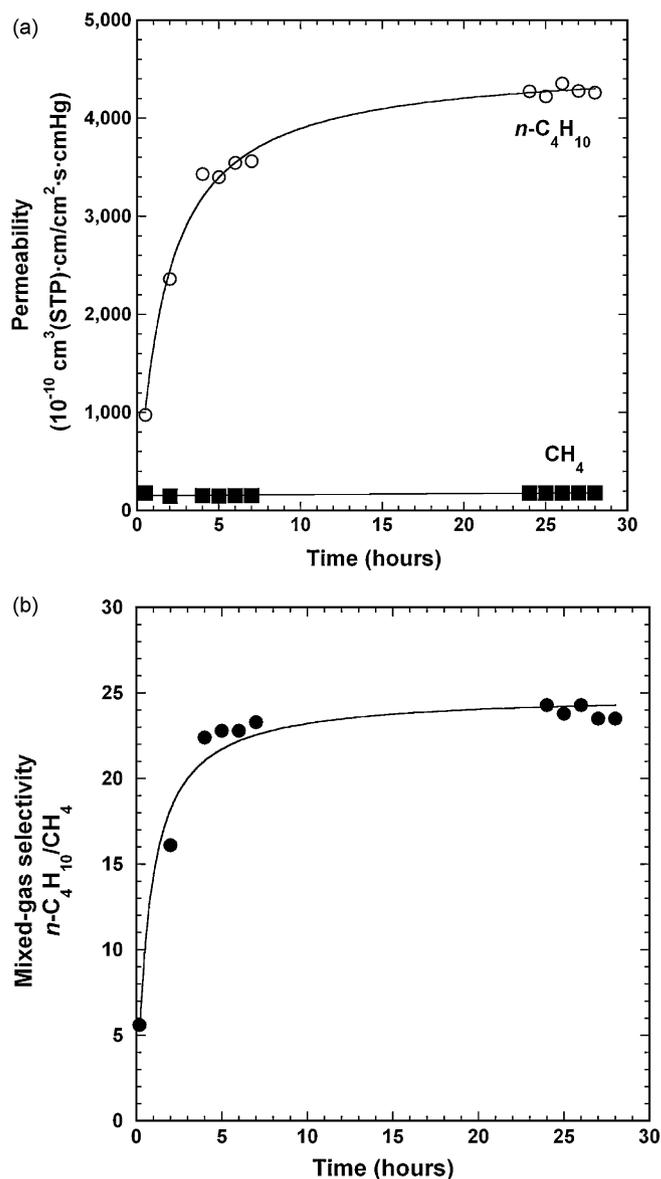


Fig. 5. (a). Mixed-gas methane and *n*-butane permeability of PIM-1 as function of permeation time. Feed composition: 2 vol.% *n*-butane/98 vol.% methane; feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); $T = 25^\circ\text{C}$. (b). Mixed-gas *n*-butane/methane selectivity of PIM-1 as function of permeation time. Feed composition: 2 vol.% *n*-butane/98 vol.% methane; feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); $T = 25^\circ\text{C}$.

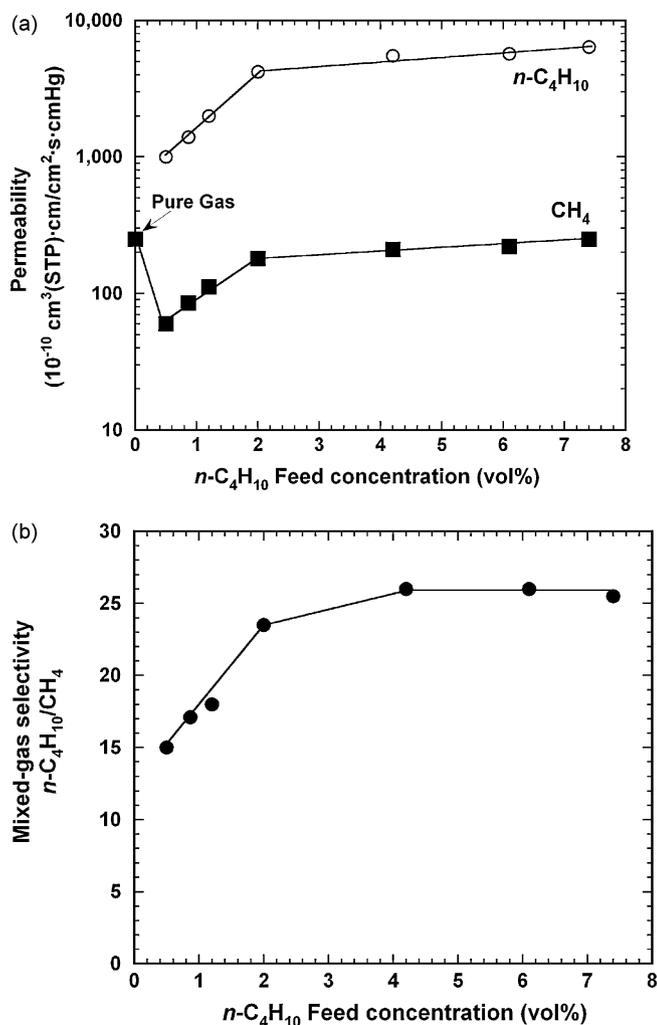


Fig. 6. (a) Mixed-gas methane and *n*-butane permeability of PIM-1 as function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); $T=25^\circ\text{C}$. (b). Mixed-gas *n*-butane/methane selectivity of PIM-1 as function of *n*-butane feed concentration. Feed pressure: 150 psig; permeate pressure: atmospheric (0 psig); $T=25^\circ\text{C}$.

this behavior. This hypothesis is supported by recent PALS studies, which showed that individual free volume elements, as well as the fraction of larger free volume elements, are smaller in PIM-1 than in PTMSP [43].

The steady-state mixed-permeation properties of PIM-1 were also studied as a function of the *n*-butane concentration in the feed mixture. Mixtures of 0.5–7.4 vol.% *n*-butane in methane were used to perform the experiments. The *n*-butane and methane permeabilities and the *n*-butane/methane selectivity of PIM-1 as function of the feed composition are shown in Fig. 6a and b, respectively. As the *n*-butane feed concentration increases from 0.5 to 2 vol.%, the *n*-butane permeability increases 5-fold, whereas the methane permeability only doubles. This increase in permeability resulted from swelling-induced dilation of PIM-1 by *n*-butane. The increase in *n*-butane/methane selectivity with increasing *n*-butane concentration in the feed mixture is due to a decrease in methane/*n*-butane diffusivity selectivity. Indeed, swelling affects both *n*-butane and methane diffusion, but it is the diffusivity coefficient of the largest molecule, i.e., *n*-butane, that increases the most. When the *n*-butane feed concentration increases from 2 to 7.4 vol.%, both methane and *n*-butane permeability reach a plateau value. For a mixture containing 7.4 vol.% *n*-butane in methane, the *n*-butane and methane permeabilities are about 6400 and 250

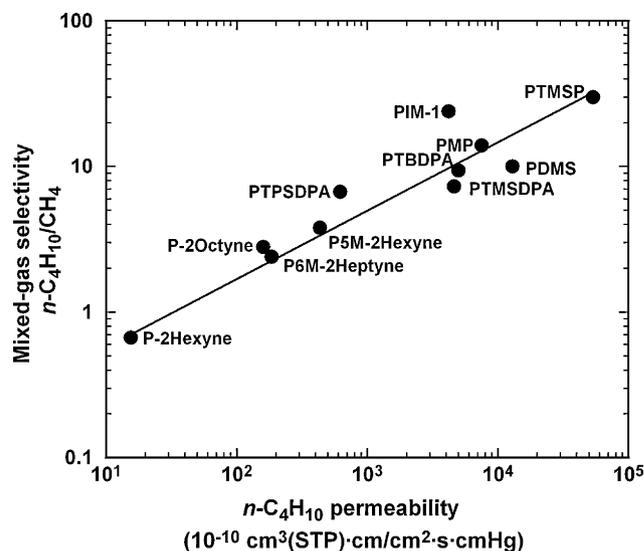


Fig. 7. Relationship between mixed-gas *n*-butane permeability and *n*-butane/methane selectivity for a series of glassy acetylene-based polymers, glassy PIM-1 and rubbery PDMS. All experiments were performed at: feed composition: 2 vol.% *n*-butane/98 vol.% methane; feed pressure: 150 psig; permeate pressure 0 psig; $T=25^\circ\text{C}$ [49].

Barrer, respectively, coupled with an *n*-butane/methane selectivity of 25.

Previously, it was reported that in organic vapor/permanent gas separations, polymeric membranes, that show the highest organic vapor permeability, also have the highest organic vapor/permanent-gas selectivity [7,19,49]. This trend is opposite to the typical permeability/selectivity trade-off proposed by Robeson for the separation of small permanent gases, such as oxygen/nitrogen and carbon dioxide/methane, where high permeability is typically coupled with a low selectivity and vice versa [44,45].

Fig. 7 shows the mixed-gas *n*-butane/methane selectivity as a function of *n*-butane permeability for PIM-1, a series of acetylene-based polymers, and rubbery PDMS [49]. PIM-1 has lower *n*-butane permeability but a higher *n*-butane/methane selectivity than rubbery PDMS, the only commercial material used for this application. Although the PIM-1 mixed-gas permeation values are slightly lower than those of PTMSP, PIM-1 offers the advantage of much better chemical stability and solvent resistance towards hydrocarbons.

4. Conclusions

PIM-1 is a rigid, glassy, high-free-volume, spirobisindane-based polymer with excellent chemical stability and good solvent resistance. Because of its high excess free volume ($FFV=0.26$), it is one of the most permeable polymers known. Unlike high-free-volume acetylene-based polymers, which have high permanent-gas permeability coupled with low permanent gas selectivity, PIM-1 has high permanent-gas permeability with moderate permanent-gas selectivity. Our study demonstrates that PIM-1 has excellent properties for *n*-butane/methane separation; the *n*-butane/methane selectivity of about 25 is similar to that of microporous PTMSP and about 2.5-fold higher than that of PDMS, the only commercial rubbery membrane material for this application. Because PIM-1 has much better chemical resistance to hydrocarbons than PTMSP, this novel polymer shows promising potential as a microporous polymeric membrane material for higher-hydrocarbon/methane separation in natural gas applications.

Acknowledgements

The authors gratefully acknowledge support of this work by the Department of Energy through the Small Business Innovation Research Program (Grant Number DE-FG02-05ER84243), and partial support through the Climate Change Technology and Innovation Initiative, Greenhouse Gas project (CCTII, GHG).

References

- [1] W.J. Koros, G.K. Fleming, Membrane-based gas separation, *J. Membr. Sci.* 83 (1993) 1–80.
- [2] J.M.S. Hennis, Commercial and practical aspects of gas separation membranes, in: D.R. Paul, Y. Yampol'skii (Eds.), *Polymeric Gas Separation Membranes*, CRC Press, Boca Raton, FL, 1994, pp. 441–512.
- [3] R.W. Baker, Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res.* 41 (2002) 1393–1411.
- [4] R.W. Baker, K. Lokhandwala, Natural gas processing with membranes: an overview, *Ind. Eng. Chem. Res.* 47 (2008) 2109–2121.
- [5] J. Schultz, K.V. Peinemann, Membranes for separation of higher hydrocarbons from methane, *J. Membr. Sci.* 110 (1996) 37–45.
- [6] M. Anand, M. Langsam, M.B. Rao, S. Sircar, Multicomponent gas separation by selective surface flow (SSF) and poly-trimethylsilylpropyne (PTMSP) membranes, *J. Membr. Sci.* 123 (1997) 17–25.
- [7] B. Freeman, I. Pinnau, Separation of gases using solubility-selective polymers, *TRIP* 5 (1997) 167–173.
- [8] T.C. Merkel, B.D. Freeman, R.J. Spontak, Z. He, I. Pinnau, P. Meakin, A.J. Hill, Ultra-permeable, reverse-selective nanocomposite membranes, *Science* 296 (2002) 519–522.
- [9] T. Masuda, E. Isobe, T. Higashimura, Polymerization of 1-(trimethylsilyl)-1-propyne by halides of niobium(V) and tantalum(V) and polymer properties, *Macromolecules* 18 (1985) 841–845.
- [10] H. Odani, T. Masuda, Design of polymer membranes for gas separation, in: N. Toshima (Ed.), *Polymers for Gas Separation*, VCH Publishers, Inc., New York, NY, 1992, pp. 107–144.
- [11] T. Masuda, Y. Iguchi, B.-Z. Tang, T. Higashimura, Diffusion and solution of gases in substituted polyacetylene membranes, *Polymer* 29 (1988) 2041–2049.
- [12] K. Nagai, T. Masuda, T. Nakagawa, B.D. Freeman, I. Pinnau, Poly[1-trimethylsilyl-1-propyne] and related polymers: synthesis, properties and functions, *Prog. Polym. Sci.* 26 (2001) 721–798.
- [13] J. Rouquerol, D. Avnir, C.W. Fairbridge, D.H. Everett, J.N. Pernicone, J.D.F. Ramsay, K.S.W. Sing, K.K. Unger, Recommendation for the characterization of porous solids, *Pure Appl. Chem.* 66 (1994) 1739–1758.
- [14] L.A. Pessan, W.J. Koros, J.C. Schmidhauser, W.D. Richards, Gas transport properties of polymers based on spirobiindane bisphenol, *J. Polym. Sci. Polym. Phys.* 33 (1995) 487–494.
- [15] J.S. McHattie, W.J. Koros, D.R. Paul, Gas transport properties of polysulphones. 1. Role of symmetry of methyl group placement on bisphenol rings, *Polymer* 32 (1991) 840.
- [16] J. Bi, G.P. Simon, A. Yamasaki, C.L. Wang, Y. Kobayashi, H.J. Griesser, Effect of solvent in casting of poly(1-trimethylsilyl-1-propyne) membranes, *Radiat. Phys. Chem.* 58 (2000) 563–566.
- [17] J. Weber, Q. Su, M. Antonietti, A. Thomas, Exploring polymers of intrinsic microporosity—microporous, soluble polyamide and polyimide, *Macromol. Rapid Commun.* 28 (2007) 1871–1876.
- [18] Y.-H. Kim, H.-S. Kim, S.-K. Kwon, Synthesis and characterization of highly soluble and oxygen permeable new polyimides based on twisted biphenyl dianhydride and spirobifluorene diamine, *Macromolecules* 38 (2005) 7950–7956.
- [19] I. Pinnau, L.G. Toy, Transport of organic vapors through poly(1-trimethylsilyl-1-propyne), *J. Membr. Sci.* 116 (1996) 199–209.
- [20] I. Pinnau, C.G. Casillas, A. Morisato, B.D. Freeman, Hydrocarbon/hydrogen mixed gas permeation in poly(1-trimethylsilyl-1-propyne) (PTMSP), poly(1-phenyl-1-propyne) (PPP), and PTMSP/PPP blends, *J. Polym. Sci. Polym. Phys.* 34 (1996) 2613–2621.
- [21] I. Pinnau, C.G. Casillas, A. Morisato, B.D. Freeman, Long-term permeation properties of poly(1-trimethylsilyl-1-propyne) membranes in hydrocarbon vapor environment, *J. Polym. Sci. Polym. Phys.* 35 (1997) 1483–1490.
- [22] R.D. Raharjo, B.D. Freeman, D.R. Paul, E.S. Sanders, Pure and mixed gas CH₄ and n-C₄H₁₀ permeability and diffusivity in poly(1-trimethylsilyl-1-propyne), *Polymer* 48 (2007) 7329–7344.
- [23] R. Srinivasan, S.R. Auvil, P.M. Burbur, Elucidating the mechanism(s) of gas transport in poly(1-(trimethylsilyl)-1-propyne) (PTMSP) membranes, *J. Membr. Sci.* 86 (1994) 67–86.
- [24] L.G. Toy, Gas and hydrocarbon vapor transport properties of disubstituted polyacetylene membranes, Ph.D. Dissertation, North Carolina State University, 2001.
- [25] R.M. Barrer, J.A. Barrie, Sorption and diffusion in porous glass, *Proc. Roy. Soc. A* 213 (1952) 250–265.
- [26] R. Ash, R.M. Barrer, C.G. Pope, Flow of adsorbable gases and vapors in a microporous medium. II. Binary mixtures, *Proc. Roy. Soc. A* 271 (1963) 19.
- [27] S.D. Kelman, S. Matteucci, C.W. Bielawski, B.D. Freeman, Crosslinking poly(1-trimethylsilyl-1-propyne) and its effect on solvent resistance and transport properties, *Polymer* 48 (2007) 6881–6892.
- [28] S.D. Kelman, B.W. Rowe, C.W. Bielawski, S.J. Pas, A.J. Hill, D.R. Paul, B.D. Freeman, Crosslinking poly[1-(trimethylsilyl)-1-propyne] and its effect on physical stability, *J. Membr. Sci.* 320 (2008) 123–134.
- [29] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, Polymers of intrinsic microporosity (PIMs): robust, solution-processable organic nanoporous materials, *Chem. Commun.* (2004) 230–231.
- [30] P.M. Budd, K.J. Msayib, C.E. Tattershall, B.S. Ghanem, K.J. Reynolds, N.B. McKeown, D. Fritsch, Gas separation membranes from polymers of intrinsic microporosity, *J. Membr. Sci.* 251 (2005) 263–269.
- [31] N.B. McKeown, P.M. Budd, K.J. Msayib, B.S. Ghanem, H.J. Kingston, C.E. Tattershall, S. Makhseed, K.J. Reynolds, D. Fritsch, Polymers of intrinsic microporosity (PIM): bridging the void between microporous and polymeric materials, *Chem. Eur. J.* 11 (2005) 2610–2620.
- [32] P.M. Budd, N.B. McKeown, D. Fritsch, Free volume and intrinsic microporosity in polymers, *J. Mater. Chem.* 15 (2005) 1977–1986.
- [33] N.B. McKeown, P.M. Budd, D. Fritsch, Thin layer composite membrane, WO Patent 2005/113,121 (2005).
- [34] N.B. McKeown, P.M. Budd, Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage, *Chem. Soc. Rev.* 35 (2006) 675–683.
- [35] P.M. Budd, N.B. McKeown, D. Fritsch, Polymers of intrinsic microporosity (PIMs): high free volume polymers for membrane applications, *Macromol. Symp.* 245–246 (2006) 403–405.
- [36] N.B. McKeown, B. Gahnem, K. Msayib, P.M. Budd, C. Tattershall, K. Mahmood, S. Tan, D. Brook, H.W. Langmi, A. Walton, Towards polymer-based hydrogen storage materials: engineering ultramicroporous cavities within polymers of intrinsic microporosity, *Angew. Chem. Int. Ed.* 45 (2006) 1804–1807.
- [37] N. Du, J. Song, G.P. Robertson, I. Pinnau, M.D. Guiver, Linear high molecular weight ladder polymer via fast polycondensation of 5,5',6,6'-tetrahydroxy-3,3',3',3'-tetramethylspirobisindane with 1,4-dicyanotetrafluorobenzene, *Macromol. Rapid Commun.* 29 (2008) 783–788.
- [38] K. Nagai, L.G. Toy, B.D. Freeman, M. Teraguchi, T. Masuda, I. Pinnau, Gas permeability and hydrocarbon solubility of poly[1-phenyl-2-[p-(triisopropylsilyl)phenyl]acetylene], *J. Polym. Sci., Part B: Polym. Phys.* 38 (2000) 1474–1484.
- [39] A.J. Hill, S.J. Pas, T.J. Bastow, M.I. Bugar, K. Nagai, L.G. Toy, B.D. Freeman, Influence of methanol conditioning and physical aging on carbon spin-lattice relaxation times of poly(1-trimethylsilyl-1-propyne), *J. Membr. Sci.* 243 (2004) 37–44.
- [40] P.M. Budd, N.B. McKeown, B.S. Ghanem, K.J. Msayib, D. Fritsch, L. Staranikova, N. Belov, O. Sanfirova, Y. Yampol'skii, V. Shantarovich, Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: polybenzodioxane PIM-1, *J. Membr. Sci.* 325 (2008) 851–860.
- [41] D.W. van Krevelen, *Properties of Polymers*, 3rd ed., Elsevier, Amsterdam, 1990, p. 71.
- [42] V.P. Shantarovich, T. Suzuki, Yu.P. Yampol'skii, P. Budd, V.V. Gustov, I.B. Kevdina, A.V. Pastukhov, S.S. Berdonosov, V.E. Bozhel'nov, Positronium annihilation data and actual free-volume distribution in polymers, *High Energy Chem.* 41 (2007) 370–380.
- [43] C.L. Staiger, S.J. Pas, A.J. Hill, C.J. Cornelius, Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer, *Chem. Mater.* 20 (2008) 2606–2608.
- [44] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.* 62 (1991) 165–185.
- [45] L.M. Robeson, The upper bound revisited, *J. Membr. Sci.* 320 (2008) 390–400.
- [46] J. Song, N. Du, G.P. Robertson, Y. Dai, M.D. Guiver, S. Thomas, I. Pinnau, Linear high molecular weight ladder polymers by optimized polycondensation of tetrahydroxytetramethylspirobisindane and 1,4-dicyanotetrafluorobenzene, *Macromolecules* 41 (2008) 7411–7417.
- [47] N. Du, G.P. Robertson, J. Song, I. Pinnau, S. Thomas, M.D. Guiver, Polymers of intrinsic microporosity (PIMs) containing trifluoromethyl and phenylsulfone groups as materials for membrane gas separation, *Macromolecules* 41 (2008) 9656–9662.
- [48] M.B. Moe, W.J. Koros, H.H. Hoehn, G.R. Husk, Effects of film history on gas transport in a fluorinated aromatic polyimide, *J. Appl. Polym. Sci.* 36 (1988) 1833–1846.
- [49] I. Pinnau, Z. He, T. Masuda, T. Sakaguchi, Pure- and mixed-gas permeation properties of poly(*p-tert*-butyl diphenylacetylene), in: I. Pinnau, B.D. Freeman (Eds.), *Advanced Materials for Membrane Separations*, ACS Symposium Series 876, American Chemical Society, Washington, DC, 2004, pp. 167–176.
- [50] J. Qiu, J. Zheng, K.V. Peinemann, Gas transport properties in a novel poly(trimethylsilylpropyne) composite membrane with nanosized organic filler trimethylsilylglucose, *Macromolecules* 39 (2006) 4093–4100.
- [51] L.M. Costello, W.J. Koros, Effect of structure on the temperature dependence of gas transport and sorption in a series of polycarbonates, *J. Polym. Sci. Polym. Phys.* 32 (1994) 701–713.
- [52] I. Pinnau, Z. He, Pure- and mixed-gas permeation properties of polydimethylsiloxane for hydrocarbon/methane and hydrocarbon/hydrogen separation, *J. Membr. Sci.* 244 (2004) 227–233.