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# Polymer materials for solving actual problems of membrane gas separation

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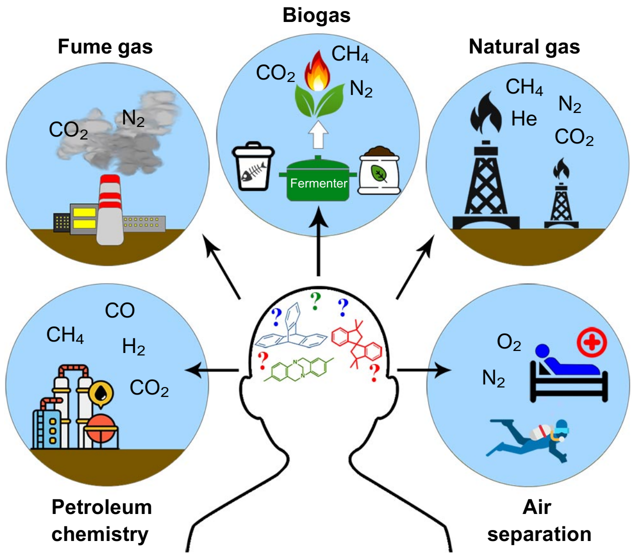
Membrane gas separation using polymeric membranes is one of rapidly developing energy-conserving technologies. This review describes the scope of membrane gas separation problems and demonstrates the relevance of membrane methods for their solution. The basic concepts and regularities of diffusion gas transfer and principles and characteristics of membrane gas separation are considered. The main physicochemical approaches to the selection of membrane materials considering both the properties of the gas–polymer system and the structure and physical properties of polymers are discussed. The considered issues are combined within a common approach to substantiate the choice of both existing commercial polymers and advanced polymeric materials to address important gas separation problems such as separation of air components; carbon dioxide, hydrogen and helium recovery from natural and industrial gas mixtures; and separation of a nitrogen and methane mixture. The avenues of development of the membrane materials science to solve each of the mentioned problems of membrane gas separation are demonstrated. The review is intended for specialists in the synthesis and physics of polymers for planning the research and assessing the applicability of polymeric materials for various practical gas separation problems and for specialists in the membrane materials science and membrane technology.
The bibliography includes 165 references.



*Keywords*: polymers, membranes, permeability, selectivity, gas separation.

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## 1. Introduction

Technologies of gas mixture separation by polymer membranes have been actively developed since the mid-1970s. Particularly in this period, asymmetric membranes with a non-porous selective layer based on poly(vinyltrimethylsilane) (PVTMS)[1,2] and on polysulfone (PSF)[1–3] appeared almost simultaneously to be used for separation of oxygen/nitrogen mixtures as air components and for hydrogen recovery in ammonia synthesis. Currently, membrane gas separation is one of the most rapidly developing and knowledge-intensive fields of membrane technology. In this field, various problems are solved mainly using asymmetric or composite membranes based on both glassy and rubbery synthetic polymers with selective layers several tens to several hundreds of nanometres thick.[2–4] The manufacture

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of these membranes is a separate problem. To address this problem, it is necessary to have a selection of known polymers, or synthesize new polymers possessing optimal separating behaviour and optimal characteristics such as molecular weight distribution, mechanical strength, chemical and thermal stability, cost, *etc.*[2–4] Currently, most membranes are manufactured on the basis of commercial mass-produced polymers.[3,4] The requirements to materials for various gas separation purposes are considerably different. For example, one of the traditional processes of separation of air components (production of technical-grade nitrogen and oxygen-enriched air) does not require high thermal stability or mechanical strength, since the process takes place at a low pressure drop and at ambient temperature. In this case, the most important parameters are gas separation characteristics of the proper membrane and the process parameters; therefore, this task can be accomplished with a broad range of polymers (Table 1, Fig. 1), such as PVTMS, PSF, tetrabromo-polycarbonate (TBPC), polyphenylene oxide (PPO), polyimides (PIs) and so on. Meanwhile, another traditional problem, hydrogen recovery during the ammonia synthesis, requires the use of thermally and chemically stable and mechanically strong polymers, for example PIs, because this process occurs at elevated temperatures and pressures in the presence of ammonia traces. The large-scale recovery of acid gases ($CO_2$, $H_2S$) from natural gas has been implemented since the early 1980s with cellulose acetate (CA), membranes, the main advantages of which are low cost and ready availability of the polymer. However, in recent years, $CO_2$-selective polymers such as poly(ethylene oxide) copolymers, PEBAX or PolyActive have been considered to be most promising for $CO_2$ recovery (see Fig. 1). The recovery of $C_2-C_4$ hydrocarbons from natural and associated gases is performed using membranes made of rubbery polymers: polydimethylsiloxane (PDMS) or other polysiloxanes (see Fig. 1);[3,5] however, there is an alternative trend that implies the use of highly permeable polyacetylenes such as polytrimethylsilylpropyne (PTMSP), but this trend is held up by the instability of the membrane material properties with time.[3] Quite a few gas separation problems related to the use of polymer membranes have not yet been solved. For example, nitrogen recovery from natural gas or biogas has not been practically implemented as yet, but is at the stage

**Table 1**. Main gas separation problems and membrane materials to address these problems.[2–5]

| Separation problem | Target component/process | Target gas pair | Polymeric material of the membrane | Progress |
|---|---|---|---|---|
| Air separation | Air: $N_2$ (technical grade, up to 99%) or $O_2$-enriched ($[O_2] = 30-50\%$) | $O_2/N_2$ | PVTMS,[a] PSF, PI, TBPC, PPO | Manufacture, laboratory research |
| Helium recovery | Helium recovery from natural gas | $He/CH_4$ | PI, perfluorinated polymers | Manufacture, pilot units, laboratory research |
| Separation of hydrogen-containing mixtures | Hydrogen recovery in ammonia synthesis; | $H_2/N_2$ | PVTMS,[a] PSF, PI | Manufacture |
| | Control of the synthesis gas composition in the methanol synthesis; | $H_2/CO$ | PSF, PI | Manufacture |
| | Hydrogen recovery in petroleum refining and petrochemical processes; | $H_2/CH_4$ | PI | Manufacture, pilot units, laboratory research |
| | Hydrogen recovery from synthesis gas | $H_2/CO_2$ | PI, CA, PBI, $CO_2$-selective polymers | Pilot units, laboratory research |
| Nitrogen removal | Nitrogen removal from natural gas and biogas | $N_2/CH_4$ | Perfluorinated polymers | Pilot units, laboratory research |
| $CO_2$ removal from gas mixtures | Purification of natural gas, biogas; | $CO_2/CH_4$ | CA, PI | Manufacture, pilot units |
| | Flue gas purification | $CO_2/N_2$ | $CO_2$-selective polymers | Pilot units, laboratory research |

[a] Currently not manufactured.

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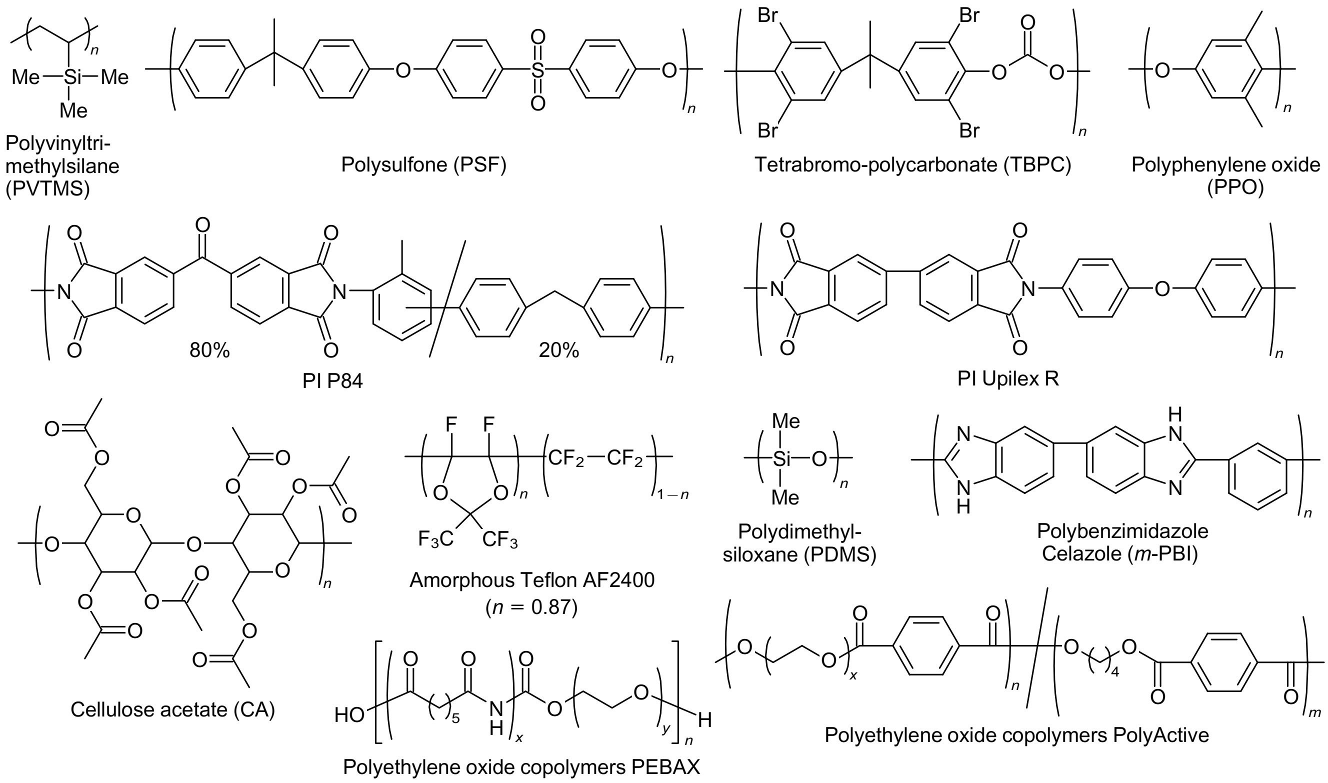


**Figure 1.** Chemical structures of the main commercial polymer membrane materials.

of laboratory research or pilot tests (see Table 1). The problem of separation of olefins and paraffins,[5] which is of crucial importance for the large-scale production of plastics, has not been solved either. As a rule, polymers with economically feasible separation characteristics for industrial implementation of membrane processes in these cases have not been found. Although only a narrow range of polymers find practical application, apart from optimization of separation designs using existing membranes, new membrane-forming polymer materials possessing separation and physicochemical characteristics needed for particular processes are being searched for, with the goal to extend the scope of practical applicability of the membrane separation technologies[3–5] (see Table 1). The main gas separation problems and some membrane materials used to solve them are presented in Table 1.[3–5] The chemical structures of the main commercial polymeric materials are depicted in Fig. 1. In this review, we consider only mixtures of non-condensable (permanent) gases, which include helium, hydrogen, oxygen, nitrogen, carbon monoxide and dioxide and methane. The issues of hydrocarbon separation are beyond the scope of this review.

## 2. Basic principles of gas permeation in polymers

Membrane gas separation implies separation of gases in a stream. The feed stream is separated into a stream that passes through the membrane (permeate), which is enriched in the more permeable component, and the stream left above the membrane (retentate), which is enriched in the less permeable component (Fig. 2).

Gas transport in polymer membranes with a thin non-porous selective layer, like that in non-porous polymer films, occurs by the dissolution–diffusion mechanism:[2–4,6,7] the gas is adsorbed on the inlet surface of the membrane (film), diffuses through the membrane under the action of the arising concentration gradient and is desorbed from the outer surface of the membrane (film).

In this case, flux $J$ through the membrane is described by Fick's law for one-dimensional diffusion in an isotropic medium. In the case of steady-state flux at a constant temperature, a linear concentration gradient in the membrane and the lack of dependence of the diffusion coefficient ($D$) on the concentration of the permeating component (which is usually the case for gases at low pressures), Fick's law is simplified to the expression[2,4,6]

$$J = D\frac{\Delta c}{l} \tag{1}$$

where $\Delta c$ is the gas concentration gradient across the membrane, $l$ is the membrane thickness. The gas concen-

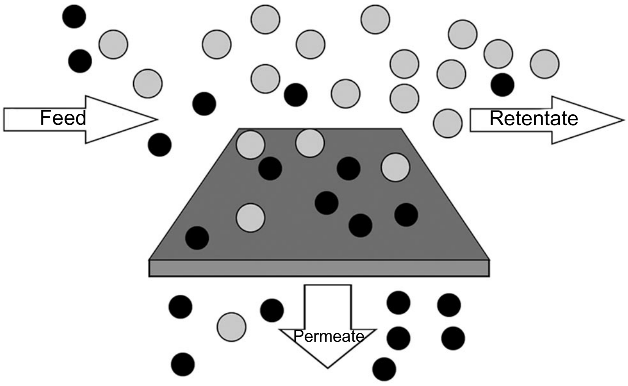


**Figure 2.** Scheme of membrane separation.

tration in the membrane is a function of pressure $c = f(p)$ according to the equilibrium isotherm of gas sorption in the membrane material. At low gas pressures, all types of isotherms are reduced to the Henry isotherm.[2,4,6] In this case, $\Delta c = S\Delta p$, where $S$ is the gas solubility coefficient in the polymer, $\Delta p$ is the pressure drop across the membrane.

Then the gas flux through the membrane is directly proportional to the pressure drop and inversely proportional to the membrane thickness

$$J = DS\frac{\Delta p}{l} \tag{2}$$

The permeability coefficient $P$ acts as the proportionality factor in this case

$$P = DS \tag{3}$$

In the membrane materials science literature, $P$ is usually expressed using arbitrary units called Barrers: 1 Barrer = $10^{-10}$ cm$^3$ (STP) cm (cm$^2$ s cm Hg)$^{-1}$. The expression is not reduced because cm$^3$ (STP) refers to the amount of permeating gas (at STP), while cm and cm$^2$ refer to polymer film characteristics. Nevertheless, there are quite a few other non-SI units, including those involving various reductions.[7] In SI units, $P$ is defined in mol (m s Pa)$^{-1}$. Membranes with unknown thickness of the selective layer are characterized by gas permeability value $Q = P/l$. In modern publications, $Q$ is measured, most often, in GPU units: 1 GPU = $10^{-6}$ cm$^3$ (STP) (cm$^2$ s cm Hg)$^{-1}$. In the membrane-related literature, $D$ is usually expressed in cm$^2$ s$^{-1}$, while $S$ is measured in either cm$^3$ (STP) (cm$^3$ cm Hg)$^{-1}$ or cm$^3$ (STP) (cm$^3$ atm)$^{-1}$. Correspondingly, in SI units, this is m$^2$ s$^{-1}$ and mol (m$^3$ Pa)$^{-1}$.

A factor characterizing the efficiency of a gas separation process is the selectivity of separation of gases $i$ and $j$

$$\alpha_{ij} = \frac{P_i}{P_j} = \frac{Q_i}{Q_j} \tag{4}$$

In view of expressions (3) and (4), gas separation selectivity (permeation selectivity, ideal selectivity or, more often, selectivity) $\alpha_{ij}$ is the product of diffusion selectivity $\alpha_{ij}^D = D_i/D_j$ and the solubility selectivity $\alpha_{ij}^S = S_i/S_j$.

The $P$, $D$ and $S$ values, the selectivity $\alpha_{ij}$, and the diffusion $\alpha_{ij}^D$ and solubility $\alpha_{ij}^S$ selectivities are considered to be parameters of the polymer–gas system at a constant temperature and moderate pressure drops.[2–4,6] The greater $P$ for more permeable component $i$ and the higher the separation selectivity for a particular pair of gases $\alpha_{ij}$, the more favourable the use of this polymer as a membrane material. However, the permeability and selectivity values follow a trade-off relationship: as the permeability increases, the selectivity decreases.[4,6] Therefore, the efficiency of a polymer material for the separation of a particular pair of gases is determined by the position in the permeability–selectivity diagrams (Robeson plots) with respect to the so-called upper bound relationship.[8–13] Since the practical applicability of a polymeric material is determined not only by its separation properties, but also by many other characteristics, the position of the polymer in the permeability–selectivity plots is a clue for further materials science research. The upper bounds in the Robeson plots are formed by polymers with the most favourable permeability/selectivity combinations and are described by the empirical relation[8,9]

$$P_i = k\alpha_{ij}^n \tag{5}$$

As time goes on, the upper bound position in these plots (Table 2) shifts to higher permeability (increase in $k$) and higher selectivity (increase in $n$), because the total number of the synthesized and studied polymers with a favourable combination of permeability and selectivity to solve various gas separation problems increases over time. The same time dependence was reported by Alentiev and Yampolskii.[14] A calculation similar to that reported by Alentiev and Yampolskii[14] carried out using the data of Table 2 shows that for the polymer with $P(O_2)$ = 100 Barrer, the $O_2/N_2$ selectivity corresponding to the upper bound increases from 4.2 at 1991 to 5.4 in 2008 and reaches 8.2 in 2015. When the polymer has $P(CO_2)$ = 100 Barrer, the $CO_2/CH_4$ selectivity corresponding to the upper bound of 1991 amounts to 34, that for 2008 is 62, and the selectivity for 2019 is 170.

Currently, the transport parameters for the polymer–gas systems have been collected into extensive databases, some of which are available to users;[15,16] in particular, the Russian database of TIPS RAS is available.[17]

Since the permeability coefficients of gases are determined by their diffusion and solubility coefficients and by their ratio, for evaluating the transport and separation capabilities of a polymer, it is important to identify the factors that affect these values. According to linear correlations known from the literature, the gas diffusion coefficients in a polymeric material depend on the effective cross-sectional area of the gas molecule, *i.e.*, on the squared kinetic diameter $d$ (Refs 18, 19)

**Table 2**. Parameters of equation (5) for Robeson upper bounds of 1991[8] and 2008[9] and current corrections (present) reported in 2015[10] and 2019.[11,12]

| Gas pair | *k*, Barrer | | | *n* | | |
|---|---|---|---|---|---|---|
| | 1991 | 2008 | present | 1991 | 2008 | present |
| $O_2/N_2$ | 389 224 | 1 396 000 | 16 700 000[a] | –5.800 | –5.666 | –5.700[a] |
| $H_2/N_2$ | 52 918 | 97 650 | 1 100 000[a] | –1.5275 | –1.4841 | –1.46[a] |
| $H_2/CH_4$ | 18 500 | 27 200 | 195 000[a] | –1.2112 | –1.107 | –1.10[a] |
| $CO_2/CH_4$ | 1 073 700 | 5 369 140 | 22 584 000[b] | –2.6264 | –2.636 | –2.401[b] |
| $CO_2/N_2$ | – | 30 967 000 | 755 580 000[b] | – | –2.888 | –3.409[b] |
| $He/CH_4$ | 5 002 | 19 800 | 67 600[c] | –0.7857 | –0.809 | –0.8[c] |
| $H_2/CO_2$ | 1 200 | 4 515 | – | –1.9363 | –2.302 | – |
| $N_2/CH_4$ | – | 2 570 | 19 900[c] | – | –4.507 | –4.6[c] |

[a] 2015 upper bound for $O_2/N_2$, $H_2/N_2$, and $H_2/CH_4$ gas pairs;[10] [b] 2019 upper bound for $CO_2/CH_4$ and $CO_2/N_2$ gas pairs;[12] [c] 2019 upper bound for perfluorinated polymers.[11]

$$\log D = K_1 - K_2 d^2 \qquad (6)$$

The solubility coefficients depend on the effective Lennard – Jones potential for the gas – gas interaction $\varepsilon/k$ (Refs 18, 19)

$$\log S = K_3 + K_4(\varepsilon/k) \qquad (7)$$

The effective kinetic diameters and the effective Lennard-Jones parameters of non-condensable gases reported in the literature [18,19] for polymers are summarized in Table 3.

Correspondingly, it follows from Eqns (3), (6) and (7) that

$$\log P = K_1 + K_3 - K_2 d^2 + K_4(\varepsilon/k) \qquad (8)$$

According to Teplyakov and Meares,[19] $K_1$ for glassy and rubbery polymers varies insignificantly, by no more than 23%. The $K_3$ value varies by no more than 46%, which is also not much. A greater contribution to $P$ is made by the product $K_4(\varepsilon/k)$, since $K_4$ may vary by approximately 90% depending on the polymer structure, while $(\varepsilon/k)$ may vary 38-fold depending on the considered gas (see Table 3). The term $K_2 d^2$ makes even a greater contribution to the permeability coefficient, as $K_2$ was reported [19] to vary by a factor of 9.5 depending on the particular polymer and $d^2$ may differ by a factor of 4.3 depending on the considered gas (see Table 3).

From Eqns (4) and (8), it follows that

$$\log \alpha_{ij} = K_2(d_j^2 - d_i^2) + K_4((\varepsilon/k)_i - (\varepsilon/k)_j) \qquad (9)$$

Thus, in most cases, from the relationship between $d^2$ and $\varepsilon/k$, it can be determined for each pair of gases which of the mixture components would pass through the membrane, *i.e.*, which component would be present in higher amount in the permeate and in lower amount in the retentate. The expected selectivity level, *i.e.*, the degree of permeate enrichment (and retentate depletion) in this component, can also be estimated.

Depending on the target component of the mixture, either permeate or retentate can be the target flow. For example, when air is separated on any non-porous polymer membrane, the permeate is enriched in oxygen [$\alpha(O_2/N_2) > 1$], because $d(O_2) < d(N_2)$ and $\varepsilon/k(O_2) > \varepsilon/k(N_2)$. Consequently, for the production of technical-grade nitrogen, the target flow is the retentate. Since air contains 78% nitrogen and only 21% oxygen, the retentate can be easily depleted in oxygen even at a moderate gas separation selectivity.[2–4,6] Thus, to attain this goal, the polymer with the highest permeability is most advantageous for air separation, all other conditions being equal. When hydrogen-containing mixtures formed in ammonia synthesis are separated, hydrogen is the target product, while unreacted nitrogen is the main contaminant. According to the data of Table 2, $d(H_2) \ll d(N_2)$ and, hence, $d^2(N_2)$ is two times greater than $d^2(H_2)$; however, $\varepsilon/k(H_2) < \varepsilon/k(N_2)$. Nevertheless, the $\varepsilon/k(N_2)$ and $\varepsilon/k(H_2)$ values differ by 25% (see Table 2), *i.e.*, the difference between $\varepsilon/k$ cannot counterbalance the difference between the squared kinetic diameters; therefore, hydrogen as the more permeable component tends to enrich the permeate. In view of the fact that hydrogen content in the mixture is about 60%,[20] the polymer with the highest gas separation selectivity is most advantageous, all other conditions being equal.

**Table 3**. Effective kinetic diameters ($d$) and effective Lennard – Jones parameters ($\varepsilon/k$) of non-condensable gases for polymers.[18,19]

| Gas | He | $H_2$ | $O_2$ | $N_2$ | CO | $CO_2$ | $CH_4$ |
|---|---|---|---|---|---|---|---|
| $d$, Å | 1.78 | 2.14 | 2.89 | 3.04 | 3.04 | 3.02 | 3.18 |
| $(\varepsilon/k)$, K | 9.5 | 62.2 | 112.7 | 83.0 | 102.3 | 213.4 | 154.7 |

In this review, we use both the positions of polymers in the permeability – selectivity plots and the relationships between $d^2$ and $\varepsilon/k$ for the specified gas pairs according to Eqn (9) to evaluate the applicability of existing commercial polymers and prospective materials, including those studied since 2018, for the solution of practical problems of gas separation.

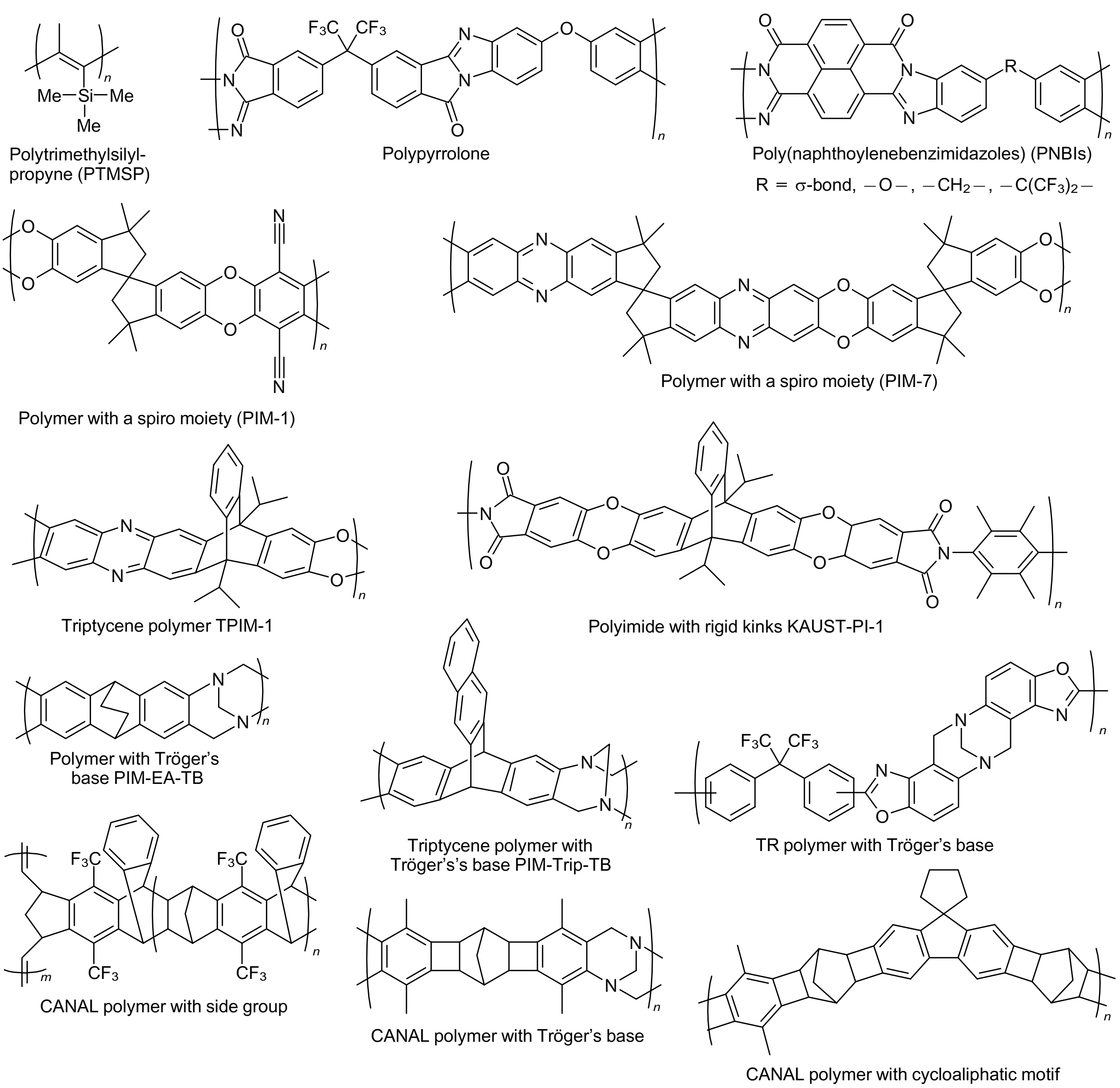
## 3. Polymeric materials for the separation of air components

The separation of air components and, in particular, nitrogen production from air, occupies a special place among membrane gas separation processes. Thus, production of nitrogen-enriched mixtures accounts for more than 50% of the market of membrane gas separation technologies.[5,21] The ready availability of raw material, the ease of obtaining these mixtures in the retentate, moderate requirements to the membrane material [22] and the wide scope of applicability of nitrogen mixtures [22–24] are responsible for the prevalence of this technology. For example, mixtures containing 90 to 98% nitrogen are used for the storage of various foodstuffs. A nitrogen content of 95% is sufficient to form an inert atmosphere for power engineering, for soldering in electronics, for processing of plastics and in chemical reactors. Mixtures containing 90 to 95% nitrogen form a fire-safe atmosphere; therefore, these nitrogen mixtures are used for filling fuel tanks, tankers and pipelines. For the storage of drugs and in metal working, 97% content of nitrogen is needed, while laser cutting requires 99.9%.[23] The technical-grade nitrogen of various concentrations is used in synthesis gas production processes.[24] In all of the above cases, one-, two- or three-stage process designs are implemented, depending on the membrane material and the required purity of the resulting gas.[22]

Today, the commercial-scale production of oxygen is mainly performed by cryogenic and adsorption methods, including the short-cycle adsorption process, as these methods provide high productivity and the required purity of oxygen at a relatively low oxygen concentration in the initial mixture. Meanwhile, according to feasibility studies,[25] small-scale production of oxygen-enriched mixtures, for example, for medicine and agriculture, could also be effectively performed by membrane separation methods,[26] particularly using polymer membranes with a non-porous selective layer.[27,28] Furthermore, for small-scale processes, important factors are the compactness and mobility of the production units, which is provided by the application of membrane technologies and combinations of membranes with other types of separation and purification methods. Currently, mixtures enriched in oxygen by means of membrane technologies are used in therapeutic and preventive medicine (24 – 82%) and to prevent the decompression illness in divers (32 – 36%);[23] even one-stage separation process may be sufficient for this goal. However, when the required oxygen content in the mixture is 90% or more, *e.g.*, for catalyst regeneration, paper making industry, waste-water treatment, *etc.*,[23] the use of one-stage air enrichment in oxygen using polymer membranes is no longer possible.[29] Meanwhile, 90% $O_2$ purity can be attained by using two or three stages, depending on the type of the membrane.[29] Apart from polymer membranes, these processes can be implemented using inorganic (*e.g.*, carbon) membranes,[30] which provide 70% oxygen content upon one-stage treatment of air. However, the cost of these membranes significantly exceeds the cost of polymer membranes; therefore, the search for new polymeric materials and the development of new composite membranes in order to achieve economically viable results is still relevant. For example, it was shown[29] that increase in the membrane permeability, with the selectivity being maintained, leads to a very fast decrease in the cost of oxygen production without deterioration of the product purity. Meanwhile, an increase in the selectivity with invariable permeability does not affect the production cost, but increases the product purity.

Thus, the search for new polymeric materials with increased permeability and selectivity for air separation is stimulated by optimization of the production processes of both oxygen-enriched air and technical-grade nitrogen.

In the permeability – selectivity diagram (Robeson plot)[8–10] for the oxygen – nitrogen pair (Fig. 4), the position of the upper bound considerably changed as new classes of polymers were investigated. In 1991, the upper bound was defined by highly permeable polyacetylenes, in particular, PTMSP, TBPC and step-ladder polypyrrolone.[8] The upper bound of 2008 was defined by polyimides, polypyrrolones and highly permeable ladder polymers with intrinsic microporosity (PIM-1 and PIM-7)[9] (Fig. 3). Finally, in 2015, the upper bound was defined only by highly permeable semiladder polymers and polyimides based on them.[10, 31] Other polymers located near the upper bound of 2015 are ultrapermeable semiladder polymers with triptycene moieties in the backbone[12, 13, 21, 32] (see Figs 3, 4)


Polytrimethylsilylpropyne (PTMSP)

Polypyrrolone

Poly(naphthoylenebenzimidazoles) (PNBIs)

R = σ-bond, –O–, $-CH_2-$, $-C(CF_3)_2-$

Polymer with a spiro moiety (PIM-1)

Polymer with a spiro moiety (PIM-7)

Triptycene polymer TPIM-1

Polyimide with rigid kinks KAUST-PI-1

Polymer with Tröger's base PIM-EA-TB

Triptycene polymer with Tröger's's base PIM-Trip-TB

TR polymer with Tröger's base

CANAL polymer with side group

CANAL polymer with Tröger's base

CANAL polymer with cycloaliphatic motif

**Figure 3.** Synthetic polymers considered in the review.

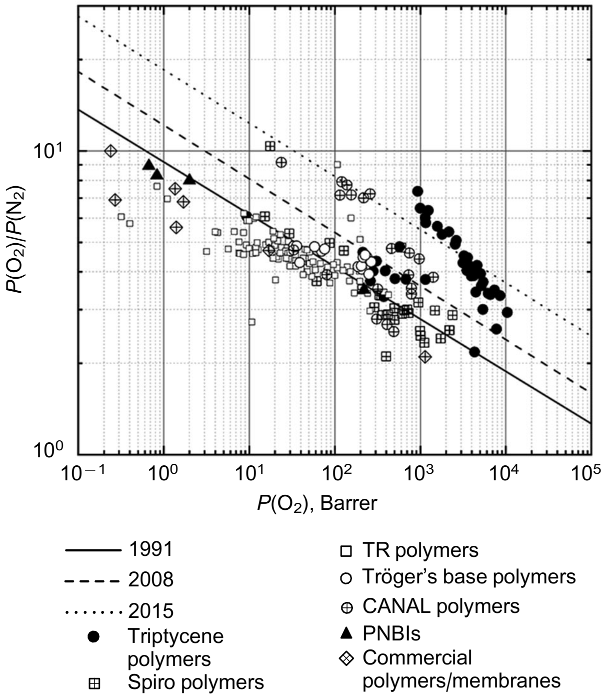


**Figure 4.** Robeson plot for $O_2/N_2$. The plot shows the upper bounds of 1991,[8] 2008 (Ref. 9) and 2015 [10] and polymers studied after 2018 and containing triptycene units,[12,13,21,32,36–38] spiro moieties [13,21,39–48] and Tröger's bases [13,21,49–52] and TR polymers,[33,37,53–63] CANAL polymers,[52,64,65] PNBIs [66] and commercial polymers [67–72] currently used for air separation membranes (see Table 4).

and some thermally rearranged (TR) polymers (rigid-chain polybenzoxazoles produced by solid-phase thermochemical reaction) with backbone kinks, *e.g.*, Tröger's bases [33] (see Figs 3, 4) and some polyimides with bulky side groups.[32,34,35]

For polyimides with bulky side groups, it is believed that the increase in the permeability is provided by increasing free volume caused by increasing hindrance of rotation of the backbone.[35] One more type of ladder polymers are so-called CANAL polymers, which combine norbornene moieties with Tröger's base units [64] or with rigid cycloaliphatic motifs [65] in the backbone (see Fig. 3). In the permeability–selectivity diagram (see Fig. 4), these polymers are located above the upper bound of 2008.[9] In the case of ladder polymers with rigid sites of contortion (kinks), this behaviour is caused by not only specific design elements leading to increased free volume and, therefore, high permeability,[13,31,32] but also enhanced diffusion selectivity,[32] resulting apparently from ordered chain packing in the polymer matrix.[32,73] Owing to particularly this effect, other semiladder polymers that are not highly permeable such as polypyrrolones [8,9] and poly(naphthoylenebenzimidazoles) (PNBIs) [66] (see Fig. 3) are also located close to the upper bounds of the 1991 and 2008 in the permeability–selectivity diagram (see Fig. 4). Indeed, PNBIs [66] are located at the upper bound of 1991 (see Fig. 4). The selectivity of the rigid semiladder polymers with kinks in the backbone tends to increase upon physical ageing due to the increase in the diffusion selectivity. For example, $\alpha^D(O_2/N_2)$ of semiladder polymers containing triptycene units in the backbone increases twofold or more as a result of physical ageing for 300–700 days.[12] In the permeability–selectivity diagram (see Fig. 4), these polymers are located above the upper bound of 2015.[10,31] The CANAL polymers with cycloaliphatic motifs [65] reach the upper bound of 2015 during the physical ageing [10,31] (see Fig. 4). This result is attributable to an approximately twofold increase in the diffusion selectivity in 55 days.[65] Apparently, these polymer units are also characterized by an ordered packing of chains in the polymer matrix formed during physical ageing,[32,73] but this issue requires further investigation.

A comparison of the data given in Fig. 4 and in Table 4 clearly evidences that none of the commercial polymers reaches even the upper bound of 1991.[8] Table 4 presents the deviations of the selectivity values ($\Delta\alpha$, %) from the upper bound of 1991,[8] which are calculated as

$$\Delta\alpha = 100\% \, \frac{\alpha - \alpha(1991)}{\alpha(1991)} \tag{10}$$

where $\alpha(1991)$ is found from known $P(O_2)$ using the upper bound equation proposed by Robeson.[8] Considering the $\Delta\alpha$ values, TBPC and PI P84 (13–15%) are located most closely to the upper bound. Meanwhile, $\Delta\alpha$ for PVTMS, which is unfortunately not manufactured now, is even lower, amounting to 9%. The deviations for PPO and Teflon AF2400 are 21–23%, while PI Upilex-R and PSF, which have been long and widely used, are characterized by the greatest $\Delta\alpha$ among the membrane polymers (36 to 40%). Although all currently used membrane materials are below the upper bound of 1991, the existence of effective processes for membrane production based on them and the stability of transport parameters over time are favourable for their use in modern industry.

The prospective membrane materials, including those shown in Fig. 2, despite their promising gas transport and separation characteristics, still have a few significant drawbacks. For example, highly permeable PTMSP, which determines the upper bound position of 1991,[8] is unstable over time and subject to physical ageing.[3,74] Meanwhile, the

**Table 4**. Modern commercial membranes for separation of air components and selective layer materials.

| Membrane | Manufacturer | Polymer | $P(O_2)$, Barrer | $\alpha(O_2/N_2)$ | $\Delta\alpha$, % (1991) | Ref. |
|---|---|---|---|---|---|---|
| Generon | HF, AS | TBPC | 1.36 | 7.5 | 14 | 67 |
| Parker | HF | PPO | 17 | 4.7 | 17 | 68 |
| Sepuran | HF | PI P84 | 0.24 | 10 | 15 | 69 |
| UBE | HF | PI Upilex-R | 0.27 | 6.9 | 40 | 70 |
| Teflon AF2400 | HF, AS | AF2400 | 1140 | 2.1 | 23 | 71 |
| PRIZM | HF | PSF | 1.4 | 5.6 | 36 | 72 |

**Note**. HF is hollow fiber, AS is asymmetric planar membrane.

synthesis of time-stable PTMSP has recently been reported;[75–77] therefore, this polymer can be considered to be promising for the production of technical-grade nitrogen. Thermally stable PNBIs,[66] which are located near the upper bound of 1991 ($\Delta\alpha = 2-9\%$) and surpass commercial polyimides in the combination of permeability and selectivity (see Table 4), are stable over time and are of great practical interest, but the manufacture of membranes from these polymers is still far from industrial implementation. Polymers containing spiro moieties[13,21,39–48] or Tröger's bases[13,21,49–52] are unstable over time,[31] and their synthesis also has not yet been sufficiently elaborated to be implemented on an industrial scale. Nevertheless, studies along this line are in progress, and at least PIM-1, which defines the upper bound of 2008,[9] is considered to be an advantageous material, in particular for the separation of air components.[21] New methods for the synthesis of PIM-1 and its copolymers[41,44,45,47,48,78] and their modifications[39,40,42,43,46,79] are being developed. The triptycene-containing polymers[12,13,21,32,36–38] and CANAL polymers[52,64,65] are considered to be interesting new materials; however, their synthesis is fairly expensive and, considering the instability of these polymers over time,[12,52,64,65] the prospects for their practical application are now obscure. Nevertheless, the situation with the synthesis of time-stable PTMSP[76] (30 years later than the primary gas separation data appeared) makes it possible to classify this group of polymers as promising materials, in particular for the separation of oxygen/nitrogen mixtures. Thermally rearranged polymers,[33,37,53–63] which arouse high interest for their gas transport characteristics, unfortunately do not currently possess the necessary mechanical characteristics for manufacture of commercial membranes; however, some of these polymers[13] may be of interest in the future.

## 4. Polymeric materials for helium recovery from natural gas

The recovery of helium from natural gas is an important engineering problem. Since the helium content in most deposits is extremely low (0.05–0.60 vol.%), it is isolated, most often, by the cryogenic method; hence, the cost of helium is quite high. According to various estimates, from a quarter to a third of the explored reserves of helium in the world are located in Russian oil and gas fields; however, the Russia's share of world helium production is about 3%. High concentrations of helium (0.15–1%) are present in the natural gas of the fields in Eastern Siberia and the Republic of Sakha (Yakutia), but cryogenic recovery of helium from helium-containing gases in Eastern Siberia is not always technologically possible or economically feasible. Thus, the use of membrane gas separation to recover helium from natural sources in Russia is a highly important goal for increasing the production of helium in Russia.

For the He/$CH_4$ pair of gases, $d(\mathrm{He}) \ll d(\mathrm{CH_4})$ (see Table 2) and, hence, $d^2(\mathrm{CH_4})$ is 3.2 times as high as $d^2(\mathrm{He})$; hence, the He diffusion coefficient is much greater than that of $CH_4$. However, the $\varepsilon/k(\mathrm{He})$ value is 16 times lower than $\varepsilon/k(\mathrm{CH_4})$ (see Table 2). In the case of medium- and low-permeability glassy polymers with high $K_2$ values,[19] the He/$CH_4$ selectivity is determined by the diffusion selectivity; therefore, helium as the more permeable component enriches the permeate, while $CH_4$ is concentrated in the retentate. Since helium concentration in natural gas is low, successful recovery of the maximum amount of helium from natural gas requires high gas separation selectivity, while the membrane permeability can often be significantly sacrificed. Therefore, the key membrane materials for the recovery of helium from natural gas are highly selective and high-strength polyimides (Table 5). Although quite a few companies attempt to use their own hollow-fiber membranes for this purpose, UBE membranes are most successful. In recent years, hollow-fiber polyimide membranes are used for He/$CH_4$ separation[80] (the membrane material is not disclosed).

In the case of rubbery (*e.g.*, PDMS[74,81]) or highly permeable glassy polymers,[17,74] for which $K_2$ in Eqn (7) is low,[19] the He/$CH_4$ selectivity is determined by high solubility of methane and can be close to 1 (Refs 12, 74) or be lower than 1.[17,74,81] For polymers located in the vicinity of the Robeson upper bound of 1991,[8] the He/$CH_4$ selectivity is close to 1 for $P$(He) of approximately 5000 Barrer, while for polymers near the Robeson upper bound of 2008,[9] it is equal to 1 for $P$(He) of approximately 19000 Barrer. These helium permeability values are quite attainable for highly permeable polyacetylenes and triptycene-based ladder polymers (see Fig. 3).[17] Thus, increase in the permeability of polymeric materials to solve the problem of helium recovery from natural gas is unreasonable, as this may invert the selectivity.

In the permeability–selectivity diagrams[8,9,11] for the helium/methane pair (Fig. 5), the position of the upper bound of 1991 was determined by highly permeable PTMSP, fluorinated polyimides and polycarbonate and by low-permeable polymethyl methacrylate.[8] The upper bound of 2008 was mainly defined by fluorinated polypyrrolones and perfluorinated amorphous polymers[9] (Fig. 6). The position of these polymers at the upper bound is usually attributed to decrease in the methane solubility in perfluorinated polymers and, hence, increase in the selectivity.[82] The effect of fluorinated groups on gas separation selectivity[83] is, in principle, explained similarly to that for perfluorinated polymers.[82] In 2019, Wu *et al.*[11] proposed a separate upper bound for the He/$CH_4$ pair of gases and perfluorinated polymers (see Fig. 5). For example, amorphous Teflons AF,[71] other perfluorodioxoles[82,84] and amorphous polyhexafluoropropylene (PHFP) and its copolymers with tetrafluoroethylene[82,85] (see Fig. 6) are located above the upper bound of 1991 and near the upper bound of 2008. Meanwhile, PHFP and its copolymers with tetrafluoroethylene annealed above the glass transition temperature are arranged above the upper bound of 2008,[82,85] thus defining the upper bound position of 2019 for perfluorinated polymers.[11] In the case of annealed PHFP, $\Delta\alpha$ value in excess of

**Table 5**. Modern commercial membranes for helium recovery from natural gas and selective layer materials.

| Membrane | Polymer | $P$(He), Barrer | $\alpha(\mathrm{He/CH_4})$ | $\Delta\alpha$ (%) (1991) | Ref. |
|---|---|---|---|---|---|
| Generon | TBPC | 17.6 | 140 | 89 | 67 |
| UBE | PI Upilex-R | 4.5[a] | 170 | 98 | 70 |
| Teflon AF2400 | AF2400 | 2740 | 6.3 | –193[b] | 71 |
| PRIZM | PSF | 13 | 49 | 97 | 72 |
| Grasis | PI | 360 GPU | 76 | – | 80 |

[a] $P$(He) was found as a rough value by the method proposed by Teplyakov and Meares.[19] [b] The negative $\Delta\alpha$(1991) means that the polymer is located above the upper bound of 1991.

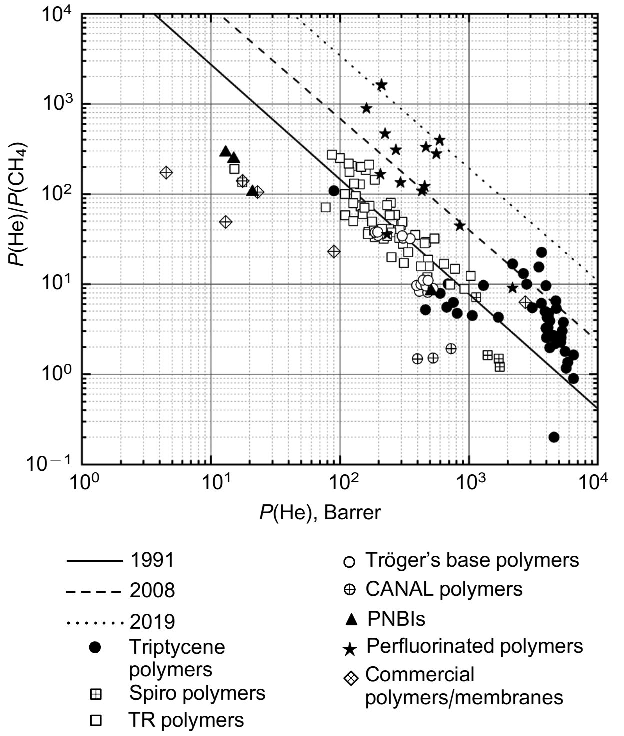


**Figure 5.** Robeson plot for He/CH$_4$. The plot shows the upper bounds of 1991,[8] 2008 (Ref. 9) and 2019 [11] and polymers studied after 2018 and containing triptycene units,[12,13,21,32,36–38] spiro moieties [13,21,39–48] and Tröger's bases,[13,21,49–52] TR polymers,[33,37,53–63] perfluorinated polymers,[84,89–92] PNBIs [66] and commercial polymers [67,70–72] currently used in membranes for helium recovery from natural gas (see Table 5).

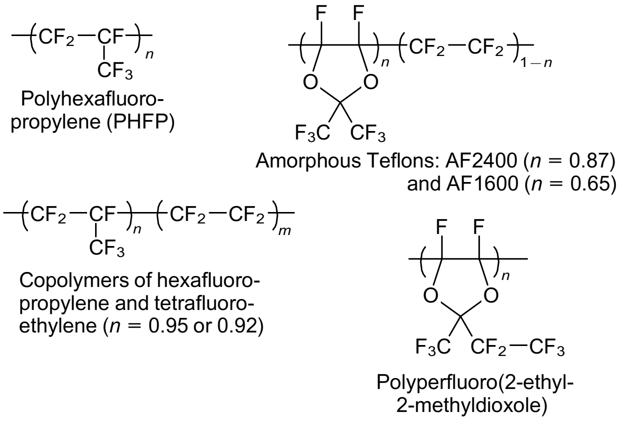


**Figure 6.** Perfluorinated amorphous polymers.

the upper bound of 2019 is approximately 170%. Nevertheless, the application of perfluorinated amorphous polymers for helium recovery from natural gas is doubtful due to their high cost, although it is beneficial, in view of high gas separation characteristics of these polymers.

A relatively cheaper method for the manufacture of fluorinated membrane materials is the surface fluorination of the membrane materials that already exist in the market; for a number of highly permeable polymers, this leads to high He/CH$_4$ selectivities virtually without the loss of productivity.[86–88] However, for large-scale processes such as the helium recovery from natural gas, this type of membrane modification has not yet found wide application.

In Table 5, $\Delta\alpha$ was calculated by Eqn (10) in which $\alpha$(1991) was found from known $P$(He) using the upper bound equation proposed by Robeson [8] (see Table 2). Comparison of the data presented in Fig. 6 and in Table 5 indicates that none of the commercial materials (except for perfluorinated AF2400) approaches the upper bound of 1991. Nevertheless, PI Upilex-R is used most widely to separate the helium/methane pair, owing to its the high selectivity, particularly in industrial modules. Although perfluorinated AF2400 lies near the upper bound of 2008, its use for the large-scale process of helium recovery from natural gas is also unreasonable due to both low selectivity and high cost of the polymer.

## 5. Polymeric materials for the separation of hydrogen-containing mixtures

The problem of hydrogen recovery from industrial gas mixtures is especially acute today in relation to industry transition to hydrogen energy production. Since the late 1970s, the key goals that have been addressed using membrane separation of hydrogen-containing mixtures were hydrogen recovery in the synthesis of ammonia and control of the synthesis gas composition in the synthesis of methanol. Both processes occur at high temperatures and pressures; therefore, even after cooling of the gas mixture down to temperatures suitable for polymer membrane technologies, it is desirable to carry out processes at high pressures (100 atm in the former case and more than 70 atm in the latter case).

A typical gas mixture in ammonia synthesis consists of 58–60% of hydrogen, approximately 25–26% of nitrogen and 15–16% of methane in the presence of residual ammonia.[20] Therefore, the most important pairs of gases that require separation in this case are $H_2/N_2$ and $H_2/CH_4$.

In the case of methanol synthesis, the initial gas mixture consists of hydrogen (more than 60%); nitrogen, carbon dioxide and methane (approximately 11% each); and carbon monoxide (more than 3%).[20] Hence $H_2/N_2$, $H_2$/CO, $H_2/CO_2$ and $H_2/CH_4$ should be considered as the target gas pairs. As a rule, in these processes, like in other petrochemical processes, residual CO$_2$ is removed by absorption methods (*e.g.*, amine treatment). When hydrogen is obtained from synthesis gas of various compositions, the first high-temperature stage ($>$700 °C; steam reforming of natural gas or gasification of coal, other natural compounds, polymer waste or pulp-and-paper waste) is followed by a lower-temperature stage (250–300 °C), that is, water gas reaction, in which the CO content in the synthesis gas can often be neglected.[93] However, the residual product contains water vapour. Hence, in this case, $H_2/CO_2$ is the target pair of gases to be separated. Naturally, it would be economically more advantageous to recover hydrogen at high temperatures; however, commercial polymer membranes are unstable at high temperatures; therefore, the gas mixture has to be cooled, which accounts for additional energy cost. Despite significant problems faced in the separation of this mixture using polymer membranes, the possible approaches developed in recent years are discussed below.

### 5.1. Polymers for the separation of $H_2/CH_4$ mixtures

The $H_2/CH_4$ pair of gases is characterized by $d(H_2) \ll d(CH_4)$ (see Table 2). Thus, $d^2(CH_4)$ is 2.2 times higher than $d^2(H_2)$ and, hence, the diffusion coefficient of $H_2$ is greater than that of $CH_4$ by a large factor. However, the $\varepsilon/k(H_2)$ value is also 2.5 times lower than $\varepsilon/k(CH_4)$ (see Table 2). Therefore, as in the case of $He/CH_4$ pair, the $H_2/CH_4$ selectivity of rubbery polymers (*e.g.*, PDMS[74,81]) or some ultrapermeable glassy polymers,[17] characterized by very low $K_2$ in Eqn (7),[19] can also be dictated by the high solubility of methane and be close to or even lower than unity.[17] In the case of polymers located near the Robeson upper bound of 1991,[8] the $H_2/CH_4$ selectivity is close to 1 for $P(H_2)$ of approximately 18 000 Barrer, while for the polymers located near the Robeson upper bound of 2008,[9] it is close to 1 for $P(H_2)$ of approximately 27 000 Barrer. Such hydrogen permeability values are known for highly permeable polyacetylenes.[17,74] In the case of medium- and low-permeable glassy polymers with high $K_2$ values,[19] the $H_2/CH_4$ selectivity is determined by the diffusion selectivity; hence, hydrogen as the more permeable component enriches the permeate, while $CH_4$ is concentrated in the retentate. If the hydrogen concentration in a mixture is high, then, as in the case of production of oxygen-enriched air, it is necessary to markedly increase the selectivity rather than to increase the $H_2$ permeability of the membrane. Thus, like in the recovery of helium from natural gas, highly selective polyimides are used most often as the materials of usually hollow-fiber membranes for the separation of hydrogen – methane mixtures (Table 6), while the use of highly permeable polymers is unreasonable.

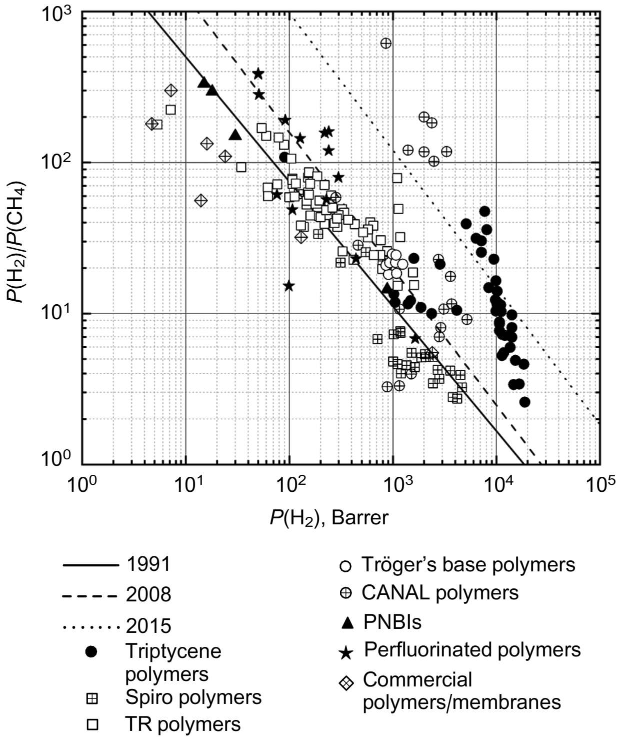


**Figure 7.** Robeson plot for $H_2/CH_4$. The plot shows the upper bounds of 1991,[8] 2008[9] and 2015[10] and polymers studied after 2018 that contain triptycene units,[12,13,21,32,36–38] spiro moieties[13,21,39–48] and Tröger's bases,[13,21,49–52] TR polymers[33,37,53–63] CANAL polymers,[52,64,65] PNBIs,[66] perfluorinated polymers[84,89–92] and commercial polymers[67–72] currently used in membranes for $H_2/CH_4$ separation (see Table 6).

In the Robeson plot[8–10,13] for the hydrogen – methane pair (Fig. 7), the position of the upper bound of 1991 was mainly defined by highly permeable polyacetylenes, in particular PTMSP, fluorinated polyimides and polymethyl methacrylate.[8] The upper bound of 2008 was defined by polyacetylenes, fluorinated polyimides and perfluorinated amorphous polymers[9] (see Fig. 6). Finally, according to the latest data of 2015 – 2020, the upper bound position is defined by semiladder polymers with kinks in the backbone[10] (see Fig. 3) and by TR polymers with similar units in the backbone[13] (see Fig. 7). The use of perfluorinated amorphous polymers is considered to be promising for the separation of both $H_2/CH_4$ and $He/CH_4$ pairs.[11] Perfluorinated polymers such as amorphous Teflons AF[71] and other perfluorodioxoles[82,84] as well as amorphous PHFP and its copolymers with tetrafluoroethylene[82,85] (see Fig. 6) are located near the upper bound of 1991. Meanwhile, PHFP and its copolymers with tetrafluoroethylene annealed above the glass transition temperature are situated above the upper bound of 2008[82,85] (see Fig. 7). For annealed PHFP, the $\Delta\alpha$ values above the upper bound of 2008 are approximately 120%. The effect of fluorine present in the polymer molecule, as in the case of $He/CH_4$ gas pair, is attributed to decreasing solubility of methane in perfluorinated polymers, while the effect of annealing is explained as being due to the sharp decrease in its diffusion coefficient. Hence, both effects lead to a pronounced increase in the selectivity.[82] Nevertheless, the application of perfluorinated polymers for the separation of $H_2/CH_4$ gas pair is restricted by their high cost. Interestingly, PNBI containing a hexafluoroisopropylidene bridge in the backbone[66] (see Fig. 3) is also beyond the upper bound of 1991 (see Fig. 7), with the

**Table 6**. Modern commercial membranes for hydrogen recovery and selective layer materials.

| Membrane | Polymer | $P(H_2)$, Barrer | $(H_2/CH_4)$ | | $\alpha(H_2/N_2)$ | | $\alpha(H_2/CO_2)$ | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | | $\alpha$ | $\Delta\alpha$, % (1991) | $\alpha$ | $\Delta\alpha$, % (1991) | $\alpha$ | $\Delta\alpha$, % (1991) | |
| Generon | TBPC | 16 | 133 | 61 | 89 | 56 | 3.6 | 61 | 67 |
| Sepuran | PI P84 | 7.2 | 300 | 54 | 300 | 12 | 6 | 57 | 69 |
| UBE | PI Upilex-R | 4.7 | 180 | 81 | 120 | 73 | 3.9 | 78 | 70 |
| Teflon AF2400 | AF2400 | 2400 | 5.5 | –2[a] | 4.3 | 43 | 0.9 | –29[a] | 71 |
| PRIZM | PSF | 14 | 56 | 85 | 56 | 75 | 2.5 | 75 | 72 |
| Proteus | – | 300 GPU | – | – | – | – | 32 | – | 107, 114 |

[a] The negative $\Delta\alpha$(1991) means that the polymer is located above the upper bound of 1991.

$\Delta\alpha$ value relative to the upper bound of 1991 being 15%. Other PNBIs lie at the upper bound of 1991.[66] The influence of fluorinated groups on the gas separation selectivity [83] is, in principle, explained similarly to that for perfluorinated polymers.[82] Polymers with fluorinated CANAL side groups [94] and fluorinated polyimides based on 6FDA dianhydride and diamines with norbornene groups, *i.e.*, CANAL-PI [52] are also located at the upper bound of 2008.[9] However, CANAL polymers containing Tröger's bases [64] and rigid cycloaliphatic motifs [65] (see Fig. 3) are located above the upper bound of 2008 [9] and, in some cases, above the upper bound of 2015 [10,31,65] (see Fig. 7). Apparently, like in the case of semiladder polymers with rigid kinks in the backbones,[12,13,21,32] this can be attributed to enhanced diffusion selectivity [32] resulting from ordering of chain packing in the polymer matrix.[32,73]

### 5.2. Polymers for the separation of $H_2/N_2$ mixtures

For the $H_2/N_2$ pair of gases, $d(H_2) \ll d(N_2)$ (see Table 2); hence, $d^2(N_2)$ is two times higher than $d^2(H_2)$ and, consequently, the diffusion coefficient of $H_2$ is much higher than the diffusion coefficient of $N_2$. However, $\varepsilon/k(H_2)$ is only 1.3 times lower than $\varepsilon/k(N_2)$ (see Table 2). Thus, the solubility of nitrogen cannot play a significant role in the $H_2/N_2$ separation selectivity, even if $K_2$ in Eqn (7) is exceptionally low.[19] Indeed, for example, for polymers located near the Robeson upper bound of 1991,[8] the $H_2/N_2$ selectivity can be equal to 1 for $P(H_2)$ of approximately 53 000 Barrer. There are no polymers with this level of hydrogen permeability coefficients.[17] As a consequence, the $H_2/N_2$ selectivity is determined by the diffusion selectivity, and hydrogen as the more permeable component is concentrated in the permeate, while $N_2$ is concentrated in the retentate. If the hydrogen concentration in hydrogen-containing mixtures is high (about 60%),[20] successful separation of the $H_2/N_2$ mixture, like separation of the $He/CH_4$ mixture, requires increase in the selectivity rather than increase in the permeability of the membrane material. Hence, as in the case of hydrogen – methane mixture, highly selective polyimides are the most promising membrane materials for the separation of $H_2/N_2$ mixtures (see Table 6). Nevertheless, as in the above cases, polysulfone membranes are used owing to their ready accessibility, relatively low cost and higher gas permeability compared to that of polyimides, despite their much lower selectivity.[20]

The upper bound of 1991 in the Robeson diagrams [8–10,13] for the hydrogen – nitrogen pair, like for the hydrogen – methane pair, was mainly defined by highly permeable polyacetylenes, in particular PTMSP, and polymethyl methacrylate.[8] The upper bound of 2008 was defined by polyacetylenes, fluorinated polyimides and highly permeable semiladder polymers with intrinsic microporosity (PIM-1 and PIM-7).[9] Finally, according to the latest data of 2015 – 2020, the upper bound position is defined by semiladder polymers containing rigid kinks [10] and by TR polymers with the same moieties [13] (Fig. 8). Perfluorinated amorphous polymers are not promising for the separation of this pair of gases, as they do not reach even the upper bound of 1991,[82,85] whereas all PNBIs are located at the upper bound of 1991 [66] (see Fig. 8). In view of the high selectivity of PNBIs and their chemical and thermal stabilities, which exceed these parameters for polyimides, these polymers can provide the basis for a selective membrane layer, especially for the hydrogen recovery in ammonia synthesis taking account of high pressure and temperature of the mixture.[20] However, the manufacture of membranes from these polymers is still far from industrial implementation. The currently studied CANAL polymers [52,64,65,94] are usually located near the upper bound of 2008 [9] (see Fig. 8). However, CANAL polymers with rigid cycloaliphatic motifs [65] go beyond the upper bound of 2015 during physical ageing.[10,31] This effect might also be attributable to an increase in diffusion selectivity and ordering of chain packing in the polymer matrix,[32,73] but this requires further investigation. The increase in the diffusion selectivity by a factor of three or more during physical ageing during 300 – 700 days is also observed for triptycene-based semiladder polymer;[12] particularly these polymers are beyond the 2015 upper bound for the $H_2/N_2$ pair.[10,31] The high selectivities of CANAL polymers containing rigid cycloaliphatic motifs,[65] observed after physical ageing [$\alpha(H_2/N_2) > 100$ for $P(H_2) > 1000$ barrer], point to their obviously good prospects. However, the problems of synthesis and stability of properties of the above polymers, like for other semiladder polymers with rigid kinks in the backbones or TR polymer, which define the Robeson upper bounds, still preclude the use of these polymers for membrane manufacturing.

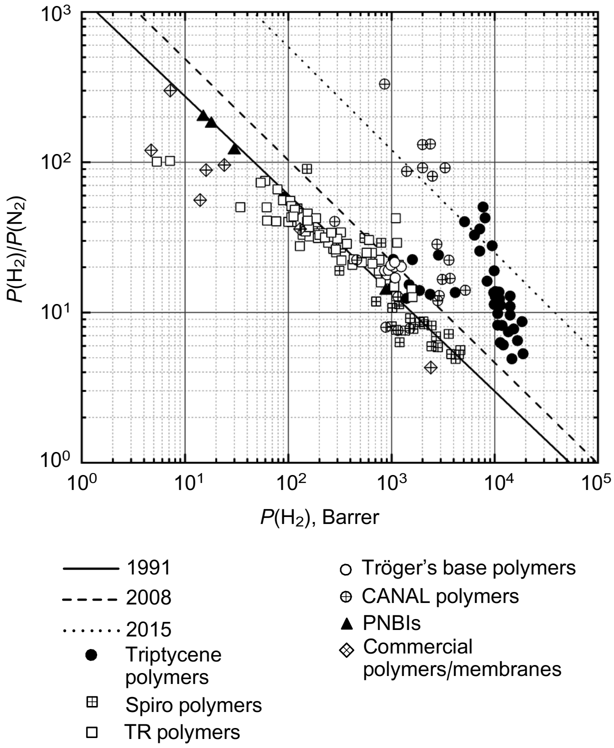


**Figure 8.** Robeson plot for $H_2/N_2$. The plot shows the upper bounds of 1991,[8] 2008 [9] and 2015 [10] and polymers studied after 2018 that contain triptycene units,[12,13,21,32,36–38] spiro moieties [13,21,39–48] and Tröger's bases,[13,21,49–52] TR polymers,[33,37,53–63] CANAL polymers,[52,64,65] PNBIs [66] and commercial polymers [67–72] currently used in membranes for $H_2/N_2$ separation (see Table 6).

### 5.3. Polymers for the separation of $H_2/CO$ mixtures

While discussing the possibility of $H_2/CO$ separation, it is necessary to note that $d(CO) = d(N_2)$ (see Table 2) and, hence, all considerations of the diffusion selectivity for the $H_2/N_2$ pair of gases are also applicable to $H_2/CO$. However, the $\varepsilon/k(CO)$ value is 20% greater than $\varepsilon/k(N_2)$ and, consequently, $\varepsilon/k(H_2)$ is 1.6 times lower than $\varepsilon/k(N_2)$ (see Table 2). Correspondingly, $P(CO) > P(N_2)$ for any polymer, and the $H_2/CO$ selectivity is lower than the $H_2/N_2$ selectivity. Moreover, according to Alentiev *et al.*,[95] if there is no specific interactions between CO and the membrane material, the CO permeability coefficient can be calculated with high accuracy *via* $P(N_2)$ by the equation

$$P(CO) = 1.476\,P(N_2)^{0.953} \quad (11)$$

Hence, the selectivity can be found as

$$\alpha(H_2/CO) = 0.678\,P(H_2)^{0.047}\,\alpha(H_2/N_2)^{0.953} \quad (12)$$

and the upper bound parameters of the permeability–selectivity plots can be found (see Table 7).

**Table 7**. Upper bounds of the permeability–selectivity plot for the $H_2/CO$ pair of gases calculated from Eqn (11).

| $k$, Barrer | | | $n$ | | |
|---|---|---|---|---|---|
| 1991 | 2008 | 2015 | 1991 | 2008 | 2015 |
| 16 000 | 30 000 | 301 000 | −1.73 | −1.68 | −1.65 |

Due to the higher solubility of CO compared to $N_2$, for polymers located near the 1991 Robeson upper bound,[8] the $H_2/CO$ selectivity may be equal to 1 for $P(H_2)$ of approximately 16 000 Barrer, while for polymers located near the 2008 Robeson upper bound,[9] it is equal to 1 for $P(H_2)$ of approximately 30 000 Barrer. For highly permeable polyacetylenes, such hydrogen permeability values are unusual, but, nevertheless, known.[17,74] Hence, like in the case of separation of other hydrogen-containing gases, the use of highly permeable polymers is unfavourable, and in this case, too, highly selective polyimides or polysulfones are used to control the synthesis gas composition (see Table 1).

Generally, if the polymer has a favourable selectivity for the $H_2/N_2$ pair of gases, it will also be applicable for the $H_2/CO$ pair, although it may be located below the upper bound of the permeability–selectivity diagram.

### 5.4. Polymers for the separation of $H_2/CO_2$ mixtures

The $H_2/CO_2$ pair of gases is most challenging for the separation on polymer membranes. However, this pair is simultaneously one of the most important, because hydrogen produced from synthesis gas always contains a large amount of $CO_2$ (up to 45%).[96]

For the $H_2/CO_2$ pair of gases, $d(H_2) \ll d(CO_2)$ (see Table 2) and, consequently, $d^2(CO_2)$ is 2 times greater than $d^2(H_2)$; hence, the $H_2$ diffusion coefficient is much greater than that of $CO_2$. However, the $\varepsilon/k(H_2)$ value is 3.4 times lower than $\varepsilon/k(CO_2)$ (see Table 2). The solubility of $H_2$ in polymers is lower than the $CO_2$ solubility to an extent such that the $H_2$ and $CO_2$ permeability coefficients for many polymers are comparable: for most polymers, the $H_2/CO_2$ selectivity does not exceed 2–4 and the Robeson plot passes through the selectivity inversion line $\alpha = 1$ (Fig. 9). For the polymers located near the Robeson upper bound of 1991,[8] the $H_2/CO_2$ selectivity can be equal to 1 for $P(H_2)$ of approximately 1200 Barrer, while for polymers located near the upper bound of 2008,[9] it is equal to 1 for $P(H_2)$ of approximately 4500 Barrer. Naturally, there are many polymers for which the $CO_2$ permeability is higher than hydrogen permeability: rubbery polymers,[74,81] highly permeable glassy polymers, *e.g.*, polyacetylenes,[74–76,97] polynorbornenes[98–106] or semiladder PIM polymers.[12,40,41,47] For these highly permeable polymers, the target component of the mixture, hydrogen, is concentrated in the retentate, while the permeate becomes enriched in $CO_2$. The recovery of hydrogen, like the enrichment of air in oxygen, requires high $CO_2/H_2$ selectivity; however, the $CO_2/H_2$ selectivity for these polymers usually does not exceed 4–5 [$\alpha(H_2/CO_2) > 0.2$][17] (see Fig. 9). The recovery of hydrogen into the permeate in the case where $\alpha(H_2/CO_2) > 1$, as for other hydrogen-containing mixtures, also requires high selectivity, but even the highest $H_2/CO_2$ selectivities known for polymers do not exceed 20, while the $P(H_2)$ values for such polymers are much lower than 10 Barrer[17] (see Fig. 9), which sharply reduces the performance of membrane processes.

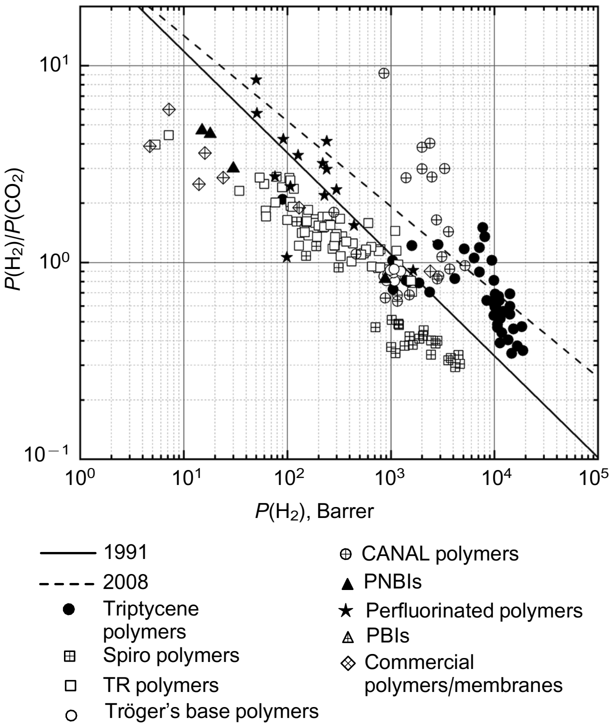


**Figure 9.** Robeson plot for $H_2/CO_2$. The plot shows the upper bounds of 1991[8] and 2008[9] and polymers studied after 2018 that contain triptycene units,[12,13,21,32,36–38] spiro moieties[13,21,39–48] and Tröger's bases,[13,21,49–52] TR polymers,[33,37,53–63] CANAL polymers,[52,64,65] PNBIs,[66] PBIs[111,119] and commercial polymers[67–72] currently used in membranes for $H_2/CH_4$ separation (see Table 6).

Thus, two strategies are used to address the $H_2/CO_2$ mixture separation: hydrogen recovery in the permeate by the diffusion mechanism and $CO_2$ recovery in the permeate owing to high $CO_2$ solubility. According to the former strategy, high-temperature gas separation at 200–300 °C on thermally stable membranes is currently considered to be promising. The principle of this separation is that the temperature factor of the permeability coefficient is significantly higher for $H_2$ than for $CO_2$. If a polymer is stable to be used at temperatures above 200 °C, it is expedient to consider this polymer for the development of high-temperature polymer membranes. Polymers proposed today for processes of this type include polyimides,[69] polybenzimidazoles (PBIs)[4,96,107] and polynaphthoylenebenzimidazoles.[66]

While choosing polymers from this series, it should be borne in mind that the use of PIs, which are hydrolyzed under drastic conditions, is unreasonable, because hydrogen-containing high-temperature mixtures contain, most often, residual amounts of water; therefore, the main efforts of researchers are now concentrated on PBIs.[107] For example, commercial *m*-PBI called Celazole (see Fig. 1), which is used to manufacture thermally stable and heat and fire resistant plastics and fibers and proton-conducting membrane matrices for high-temperature hydrogen fuel cells,[108] has barrier propertes at room temperature[107] [$P(H_2) < 1$ Barrer].[7] However, at temperatures of 200–250 °C, the permeability coefficient of hydrogen sharply increases to 14 (Ref. 7) and 23 (Ref. 109) Barrer, while the $H_2/CO_2$ selectivity reaches 20 (Ref. 7)–24 (Ref. 109). The hollow fibers based on *m*-PBI at temperatures of 200–250 °C have a hydrogen permeability of 200–400 GPU for the $H_2/CO_2$ selectivity of 20–40.[107] Recent publications describe modification of *m*-PBI by doping with phosphoric acid[110] or cross-linking.[111]

The data obtained at 150–200 °C are also far above the upper bound in the $H_2/CO_2$ plot (see Fig. 9). Other chemical structures of PBI[107,109,112] and TR polymers mixed with *m*-PBI[107,113] are no less promising. These polymers and mixtures are much more permeable than *m*-PBI and are also above the upper bound in the $H_2/CO_2$ plot (see Fig. 9). Finally, a planar composite membrane Proteus[107,114] was developed and characterized by $Q(H_2) \approx 300$ GPU and $\alpha(H_2/CO_2) \approx 32$ at 200 °C.[107] The membrane material is not disclosed, but judging from the position above the upper bound of the $H_2/CO_2$ plot (see Fig. 9),[107,114] this may also be PBI.

If the latter strategy is used, polymers should have high $CO_2/H_2$ selectivities, which are, unfortunately, unattainable for common polymers. Therefore, research in this area is focused on polymers and materials that specifically interact with $CO_2$.[96,115,116] Thus, due to the high solubility of $CO_2$ in these materials, the membrane selectivity can exceed 50 at a high performance.[96,117] Materials of this type characterized by specific interactions with $CO_2$ are discussed below. The main drawback of these materials is operating temperature, which does not exceed 100 °C; therefore, the gas mixture must be cooled before the separation. Nevertheless, both separation strategies are used today:[114] in the first, high-temperature stage, $H_2$-selective Proteus membranes are used,[107,114] while in the second, low-temperature stage, $CO_2$ is recovered from the mixture on $CO_2$-selective Polaris membranes.[118]

An interesting exception to the general rule are CANAL polymers containing rigid cycloaliphatic motifs.[65] Films of these polymers are characterized by $P(H_2)$ from 2800 to 5200 Barrer at a $H_2/CO_2$ selectivity close to 1. However, during physical ageing, the $CO_2$ permeability decreases to a substantially higher extent than hydrogen permeability. Therefore, the points corresponding to these polymers cross the selectivity inversion line, and at $P(H_2)$ from 900 to 2400 Barrer, the $H_2/CO_2$ selectivity is 4 to 9. This effect may also be attributed to an increase in the diffusion selectivity and ordering of chain packing in the polymer matrix during physical ageing,[32,73] which requires further thorough investigation. Nevertheless, these selectivities of CANAL polymers containing rigid cycloaliphatic motifs[65] in combination with high hydrogen permeability indicate that these polymers are evidently promising for the separation of the $H_2/CO_2$ pair.

In Table 6, the $\Delta\alpha$ values were calculated by Eqn (10) where $\alpha(1991)$ was found from known $P(H_2)$ using the upper bound equations proposed by Robeson[8] (see Table 2) for the corresponding pairs of gases. Comparison of the data shown in Figs 4–6 and in Table 5 indicates that only perfluorinated AF2400 for the $H_2/CH_4$ and $H_2/CO_2$ pairs is above the upper bound of 1991, but its application is unreasonable due to low selectivity. All other commercial polymers are far below the upper bound of 1991. Among commercial polymers, only PI P84 is located close to the upper bound of 1991 for the $H_2/N_2$ pair ($\Delta\alpha = 12\%$). That is why Sepuran hollow fibers are best suited for solving this problem, while the Proteus membrane is optimal for high-temperature recovery of hydrogen.

## 6. Polymeric materials for nitrogen and methane separation

The problem of nitrogen and methane gas separation is also important for increasing the calorific value of natural gas, which contains, as a rule, 4 to 10% of nitrogen and, in some cases, even 30% and more,[120] and for methane enrichment of biogas containing 5–15% of nitrogen.[96] The gas sent to a pipeline should contain less than 4% of nitrogen; the product containing 30–50% of nitrogen can be used as a compressor fuel; and the product with nitrogen content of 50–85% is suitable only as a flare gas.[120]

For the $N_2/CH_4$ pair of gases, $d(N_2)$ is smaller than $d(CH_4)$ (see Table 2), but $d^2(CH_4)$ is only 9% greater than $d^2(N_2)$; hence, the diffusion coefficient of $N_2$ is higher than the diffusion coefficient of $CH_4$, but the $N_2/CH_4$ diffusion selectivity depends most appreciably on $K_2$.[18,19] Hence, for rubbery polymers[74,81] and for highly permeable glassy polyacetylenes,[74–76,97] $\alpha^D(N_2/CH_4)$ is moderate: 1.2 for PDMS[81] and 1.1–1.3 for polyacetylenes.[17] According to Teplyakov *et al.*,[18,19] the diffusion selectivity varies from 1.2 to 6.6. However, the $\varepsilon/k(CH_4)$ value is also 1.9 times higher than $\varepsilon/k(N_2)$ (see Table 2). Therefore, the $N_2/CH_4$ solubility selectivity is always less than 1 (from 0.28 to 0.09 according to Teplyakov *et al.*[18,19]). Since the diffusion and solubility selectivities are oppositely directed and comparable in magnitude, not only the Robeson plot for the $N_2/CH_4$ pair of gases passes through the selectivity inversion line $\alpha = 1$ (Fig. 10), but also the numbers of polymer located on both sides of the inversion line are approximately equal.[9] Moreover, the nitrogen/methane separation selectivity does not exceed 7, while the methane/nitrogen selectivity does not exceed 8;[17] therefore, the separation of a nitrogen–methane mixture is quite a complicated task for polymer membranes.

Feasibility calculations show that nitrogen separation from natural gas is inexpedient if the nitrogen content is more than 30%.[120] As applied to the problem of nitrogen/methane separation, the whole array of polymeric materials is divided into nitrogen-selective (nitrogen-enriched stream in the permeate) and methane-selective materials (methane-enriched stream in the permeate).[120] Thus, nitrogen-selective polymers are advantageous for separating small amounts of nitrogen from natural gas or biogas, while methane-selective polymers are advisable for mixtures with high nitrogen contents. Methane-selective materials are usually rubbery polymers, some block copolymers, glassy polynorbornenes and highly permeable polyacetylenes.

In the Robeson plots[9,11] for the $N_2/CH_4$ pair, the upper bound position of 2008 was defined by PTMSP and its

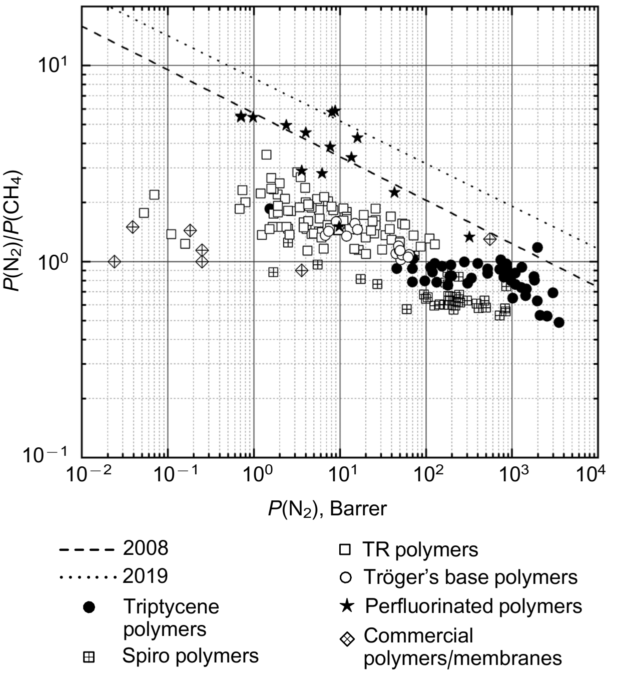


**Figure 10.** Robeson plot for $N_2/CH_4$. The plot shows the upper bounds of 2008 [9] and 2019 [11] and polymers studied after 2018 that contain triptycene moieties,[12,13,21,32,36–38] spiro moieties [13,21,39–48] and Tröger's bases,[13,21,49–52] TR polymers,[33,37,53–63] perfluorinated polymers [84,89–92] and commercial polymers.[67–72]

copolymers, fluorinated polypyrrolone and polyimide and, mainly, perfluorinated amorphous polymers.[9] As in the case of helium–methane pair, the special role of perfluorinated polymers is attributed to a decrease in the methane solubility and, hence, increase in the selectivity.[82] The beneficial effect of fluorinated groups on the selectivity is explained in a similar way.[83] In 2019,[11] a separate upper bound for perfluorinated polymers was proposed for the $N_2/CH_4$ pair (see Fig. 10). Thus, amorphous Teflon AF 2400,[71] perfluorinated methyl ethyl dioxole [82,84] and amorphous PHFP [82,85] are located at approximately the upper bound of 2008 (see Fig. 10). Meanwhile, PHFP and its copolymers with tetrafluoroethylene annealed above the glass transition temperature lie above the upper bound of 2008,[82,85] with annealed PHFP being located even somewhat higher than the 2019 upper bound for perfluorinated polymers [11] [$\Delta\alpha$(2019) is approximately 7%] (see Fig. 10). Although the use of perfluorinated polymers for nitrogen recovery from natural gas is questionable because of their high cost, they have been investigated as nitrogen-selective membranes on a pilot scale.[120] Apparently, in view of high gas-separation characteristics of perfluorinated polymers, their application for the separation of nitrogen and methane is quite promising. A less expensive method for the fabrication of nitrogen-selective membranes is surface fluorination, which provides high $N_2/CH_4$ selectivity with some loss of permeability for a number of highly permeable polymers.[86–88] Nevertheless, because of the difficulties in the design of modification process for large-area membranes, requiring a thorough selection of process conditions for the use of fluorine as a hazardous chemical, the need for special equipment stable in harsh environments, difficulty of disposal of used fluorine and so on,[86] this method of polymer membrane modification has not yet found application in practice.

Currently, pilot projects using methane-selective membranes have been developed and are being implemented to address the task of separation of nitrogen–methane mixtures. In particular, high-performance PDMS membranes are used in this process,[120] in spite of their low selectivity — $\alpha(CH_4/N_2) \approx 3$. Other commercial membranes are inapplicable for this purpose, as their $N_2/CH_4$ selectivity is close to 1.[67–72,121]

## 7. Polymeric materials for carbon dioxide recovery from industrial mixtures

### 7.1. Polymers for the separation of $CO_2/CH_4$ mixtures

The removal of acid gases from natural gas is one of the major large-scale membrane processes (see Table 1). The key trouble with this process is the release of carbon dioxide. The $CO_2$ content of natural gas is usually 20–40%,[96,115] and, in some cases, it is up to 70%.[96,115] Thus, the main pair of gases that served as the target for the selection of membrane materials is $CO_2/CH_4$.

Like in the case of the $O_2/N_2$ pair, $d(CO_2) < d(CH_4)$ (see Table 2) and, hence, the diffusion coefficient of $CO_2$ is greater than that of $CH_4$. Also, $\varepsilon/k(CO_2)$ considerably exceeds $\varepsilon/k(CH_4)$ (see Table 2); therefore, the solubility coefficient is higher for $CO_2$ than for $CH_4$. Finally, the permeability coefficient is also much higher for $CO_2$ than for $CH_4$, and the separation selectivity of $CO_2/CH_4$ pair is determined by both the diffusion and solubility selectivities. In the membrane separation of the carbon dioxide–methane mixture, the permeate is enriched in the more permeable $CO_2$, while $CH_4$ is concentrated in the retentate. This is fairly advantageous, as in the case of obtaining technical-grade nitrogen from air. Therefore, the removal of acid gases from natural gas was expectedly among the first membrane gas separation processes to be implemented and to employ, since 1980s, asymmetric planar membranes (Separex) based on cellulose acetate, a cheap polymer produced on a large scale,[3–5] despite the fact that $P(CO_2)$ for cellulose acetate does not exceed 6 Barrer.[17] When the $CO_2$ content in natural gas is high, multistage separation processes are of course necessary, which makes the separation more expensive.

One more problem requiring the separation of a $CO_2/CH_4$ mixture is the separation of biogas components, which has been especially important in recent decades with the advent of microbiological techniques (see Table 1). Biogas also contains 30–40% of $CO_2$;[96] therefore, the recovery is performed using the same membrane materials, as treatment of natural gas. One more biogas component is nitrogen (5 to 15%).[96] However, for cellulose acetate membranes, nitrogen permeability is close to methane permeability and, hence, nitrogen is also concentrated in the retentate; generally, this does not prevent the use of recovered methane for fuel, together with nitrogen impurity.[96]

In the Robeson diagram [8,9,12,13] for the carbon dioxide–methane pair (Fig. 11), like for other pairs of gases, the upper bound position has also significantly changed as new classes of polymers were studied. The upper bound of 1991 was mainly defined by highly permeable polyacetylenes, in particular PTMSP, fluorinated polyimides and poly(methyl methacrylate).[8] The 2008 upper bound was defined by polyacetylenes, fluorinated polyimides and highly permeable ladder polymers with intrinsic microporosity (PIM-1 and PIM-7).[9] Some polyimides with bulky side groups are also located near the upper bound of 2008.[34,35] Finally,

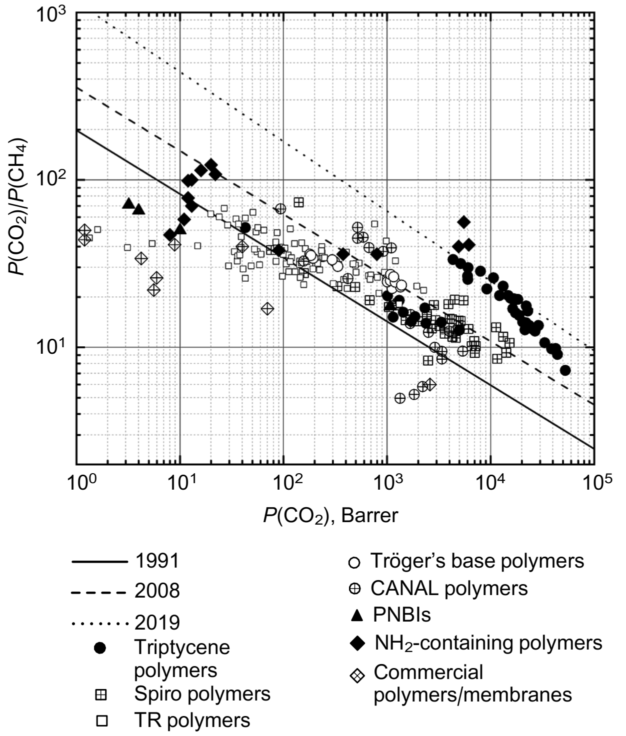


**Figure 11.** Robeson plot for $CO_2/CH_4$. The plot shows the upper bounds of 1991,[8] 2008[9] and 2019,[12] some perfluorinated polymers and polymers studied after 2018 that contain triptycene units,[12,13,21,32,36–38] spiro moieties[13,21,39–48] and Tröger's bases,[13,21,49–52] including TR polymers with respective moieties[33,37,53–63] and commercial polymers[67–72] currently used in membranes for separation of natural gas and biogas (Table 8).

according to the latest data of 2019–2020, the upper bound position is defined by highly permeable semiladder polymers, including those containing triptycene units in the backbone[12] and TR polymers with similar units[13] (see Fig. 11). As for the oxygen–nitrogen pair, this location in the plot for semiladder polymers with rigid kinks in the backbone is determined by not only the increased free volume and, hence, high permeability,[13,31,32] but also by the increased diffusion selectivity,[32] which is combined with high $CO_2$ solubility and thus leads to high separation selectivity.

CANAL polymers[52,64,65,94] are located near the 2008 upper bound.[9] And only physically aged CANAL polymers with rigid cycloaliphatic motifs[65] are above the upper bound of 2008,[9] although they still do not reach the upper bound of 2019.[12] Apparently, this can also be attributed to a sharp increase in the selectivity (from 5 to 11 within 55 days)[65] and to possible ordering of the chain packing in the polymer matrix during physical ageing.[32,73] Similar increase in the diffusion selectivity during physical ageing is observed for semiladder polymers with triptycene moieties in the backbone[12] in which $\alpha^D(CO_2/CH_4)$ increases 2–2.5-fold within 300–700 days.

Perfluorinated amorphous polymers are also considered to be promising materials for separation of $CO_2/CH_4$ pair.[11,116] Nevertheless, amorphous Teflons AF[71] and other perfluorodioxoles[82,84] (see Fig. 6) do not reach the upper bound of 1991. Meanwhile, the deviation $\Delta\alpha$ from the 1991 upper bound of amorphous PHFP is approximately 6%;[82,85] its copolymers with tetrafluoroethylene annealed above the glass transition temperature are located above the upper bound of 1991,[82,85] while annealed PHFP approaches the 2008 upper bound[82,85] (the deviation $\Delta\alpha$ from the upper bound of 2008 is also approximately 6%) (see Fig. 11). These effects are, most often, attributed by the authors to a decrease in the methane solubility in perfluorinated polymers and, hence, increase in the selectivity.[82] It is of interest that PNBI containing a hexafluoroisopropylidene bridge in the backbone[66] is also above the 1991 upper bound and approaches the 2008 upper bound. The effect of fluorinated groups on the gas separation selectivity[83] is also explained by decreasing methane solubility.[82] The application of fluorinated and perfluorinated polymers for large-scale recovery of $CO_2$ from natural gas is unlikely, because of their high cost; however, this can be cost-effective for the separation of biogas.

### 7.2. Polymers for the separation of $CO_2/N_2$ mixtures

The kinetic diameters of gas molecules in the $CO_2/N_2$ pair, which is the major gas mixture in the separation of flue gases (see Table 1), are roughly equal (see Table 2); therefore, the $d^2(CO_2)-d^2(N_2)$ difference is close to zero, the diffusion selectivity is low, differing only slightly from unity.[14] The $\varepsilon/k(CO_2)$ value is 2.6 times greater than $\varepsilon/k(N_2)$ (see Table 2); therefore, the selectivity of separation of these gases is determined by the selectivity of solubility. Like in the case of $CO_2/CH_4$ pair of gases, the permeate should be enriched in $CO_2$, while $N_2$ should be concentrated in the retentate. The $CO_2$ content in flue gases is relatively low, ranging from 8 to 15%, while the nitrogen content is 60 to 70%;[96] therefore, as in the case of production of oxygen-enriched air, it is necessary not only to increase the $CO_2$ permeability of membranes but also to considerably increase the selectivity; this can be attained only by increasing the $CO_2$ solubility in the membrane material. However, flue gases have to be cooled down before membrane separation; furthermore, they contain water vapour, sulfur oxides or nitrogen oxides, which requires additional purification. The need to include more stages retards the imple-

**Table 8**. Modern commercial membranes for carbon dioxide recovery and selective layer materials.

| Membrane | Polymer | $P(CO_2)$, Barrer | $\alpha(CO_2/CH_4)$ | $\Delta\alpha$, % (1991) | $\alpha(CO_2/N_2)$ | $\Delta\alpha$, % (2008) | Ref. |
|---|---|---|---|---|---|---|---|
| Generon | TBPC | 4.2 | 34 | 70 | 23.2 | 90 | 67 |
| Sepuran | PI P84 | 1.2 | 50 | 73 | 50 | 86 | 69 |
| UBE | PI Upilex-R | 1.2 | 44 | 76 | 29 | 92 | 70 |
| Teflon AF2400 | AF2400 | 2600 | 6 | 39 | 4.7 | 82 | 71 |
| PRIZM | PSF | 5.6 | 22 | 79 | 22 | 90 | 72 |
| Separex | CA | 5.96 | 29 | 86 | 26 | 74 | 142 |
| PolyActive | – | 40 | 17 | 84 | 40 | 18 | 143 |
| Polaris | – | 1000 GPU | – | – | 50 | – | 118 |

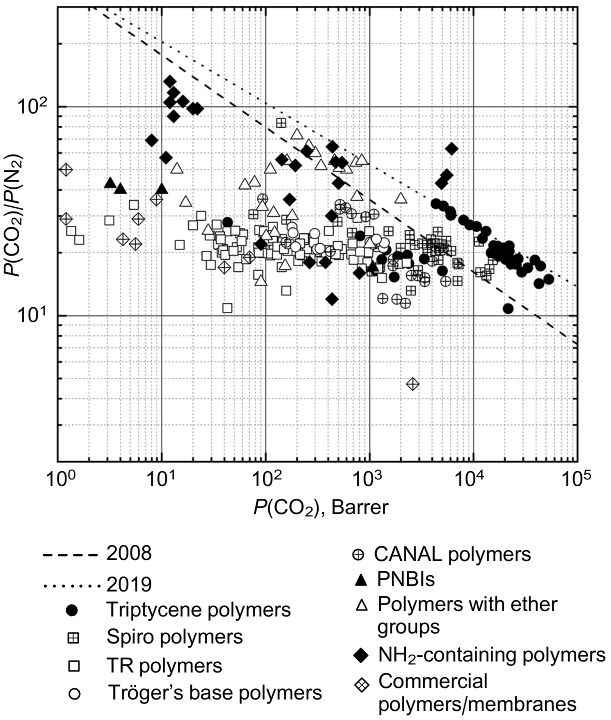


**Figure 12.** Robeson plot for $CO_2/N_2$. The plot shows the upper bounds of 2008[9] and 2019,[12] perfluorinated polymers and polymers studied after 2018 that contain triptycene units,[12,13,21,32,36–38] spiro moieties[13,21,39–48] and Tröger's bases,[13,21,49–52] including TR polymers,[33,37,53–63] polymers with ether blocks,[105,106,122–131] materials based on nitrogen-containing polymers and ionic liquids[50,132–141] and commercial polymers[67–72,142,143] (see Table 8).

mentation of the membrane gas separation for the $CO_2/N_2$ pair: only pilot units now exist. The Robeson upper bounds (Fig. 12) for the $CO_2/N_2$ gas pair are generally quite arbitrary, because the point cloud is actually extended along the permeability axis.[14] Nevertheless, the upper bound of 2008 is defined by polyacetylenes, including PTMSP, highly permeable ladder polymers with intrinsic microporosity (PIM-1 and PIM-7) and rubbery polysiloxanes and polyphosphazenes with methoxy and ethoxy groups.[9] According to the data of 2019, the upper bound position is defined by the same groups of polymers as that for the $CO_2/CH_4$ pair, namely, highly permeable semiladder polymers, including the polymers featuring triptycene units in the backbone[12,116] and TR polymers with the same units[13,116] (see Fig. 12). Nevertheless, materials in which $CO_2$ is readily soluble based on nitrogen-containing polymers, ionic liquids and polymers containing aliphatic polyether blocks have been considered in recent years particularly for the $CO_2/N_2$ pair.[96,115,116] High solubility of $CO_2$ in these polymers is determined by specific interactions between the quadrupole $CO_2$ molecule and charged or dipole groups of the polymer chain.[96,116] Since the mechanism of $CO_2$ recovery from mixtures on these membranes is equally applicable to separation of $CO_2/N_2$ mixtures and $CO_2/H_2$ mixtures, they will be considered separately.

In Table 8, $\Delta\alpha$ is calculated by Eqn (10), where $\alpha(1991)$ and $\alpha(2008)$ are found from known $P(CO_2)$ using the upper bound equations proposed by Robeson[8,9] (see Table 2) for the corresponding gas pairs. Comparison of the data shown in Figs 11 and 12 and Table 8 indicates that none of the commercial materials reaches the 1991 and 2008 upper bounds. Only polymer membranes characterized by specific interaction with $CO_2$ occupy top positions.

### 7.3. Polymeric materials with specific interactions for carbon dioxide recovery from nitrogen- and hydrogen-containing mixtures

Polymers and polymeric materials in which $CO_2$ is readily soluble, in particular those functioning according to active (facilitated) transport principles have been actively studied in recent years for the separation of $CO_2/N_2$ and $CO_2/H_2$ gas mixtures. Most of these materials can be regarded as polymers with stationary sites of complex formation with $CO_2$. Quite a few models for the transport in these systems have been developed to date;[144] however, the simplest and most useful model has been proposed by Alentiev *et al.*[96] and Rea *et al.*[144] and is based on the dual mode sorption in glassy polymers.[2,4,6,144]

According to this model, the total permeability coefficient $P$ at low pressures is defined as the sum of contributions from the passive and active transport

$$P = P_D + P_C = k_D D_D + D_C k_C \tag{13}$$

where $P_D$ is the permeability coefficient for the passive transport, $k_D$ is the solubility coefficient for the Henry population of the sorbate molecules in the polymer matrix, $D_D$ is the diffusion coefficient for the passive transport in the matrix corresponding to this population, $P_C$ is the permeability coefficient for facilitated transport, $D_C$ is the effective diffusion coefficient for the population of the specifically interacting sorbate molecules, $k_C$ is the solubility coefficient for the specifically interacting sorbate molecules. For non-interacting gases such as $N_2$ and $H_2$, the $P$ value is determined only by the first term of Eqn (13), while in the case of $CO_2$, the specific interaction can markedly increase the total solubility coefficient and, hence, the permeability; as a result, the selectivity of separation of $CO_2$-containing gas mixtures increases.

For example, $CO_2$ reacts with amino groups $-NH_2$, $-NHR$ and $-NR_2$ present in polymers such as polyvinylamine, polyallylamine, polyethyleneimine, chitosan or PAMAM (polyamidoamine dendrimer) (Fig. 13).[117] Primary and secondary amines react with $CO_2$ to form zwitter-ions and thus they act as binding sites.[145] If a membrane contains water, $CO_2$ is converted to carbonate or hydrogen carbonate ion, as in the standard amine treatment.[116] In this case, $k_C$ is determined by the concentration of nitrogen-containing groups and by the equilibrium constant for the reaction of carbon dioxide with nitrogen-containing groups.[115] However, separation processes on these membranes depend not only on the concentration of binding sites, but also on the pressure, temperature and humidity, which in some case sharply decrease the gas separation characteristics.[146,147] Nevertheless, the permeability and selectivity values for such membranes reported in original publications and reviews may be very high.[96,115,117,148] For example, poly-*N*-methylvinylamine-based membranes provide separation selectivity of up to 160 for $CO_2/H_2$ and up to 350 for $CO_2/N_2$ at $P(CO_2)$ of 6800 Barrer,[149] while poly-*N*-isopropylallylamine-based membranes[148] demonstrate a selectivity of 300 for $CO_2/H_2$ and 650 for $CO_2/N_2$ at $P(CO_2)$ of 6500 Barrer.

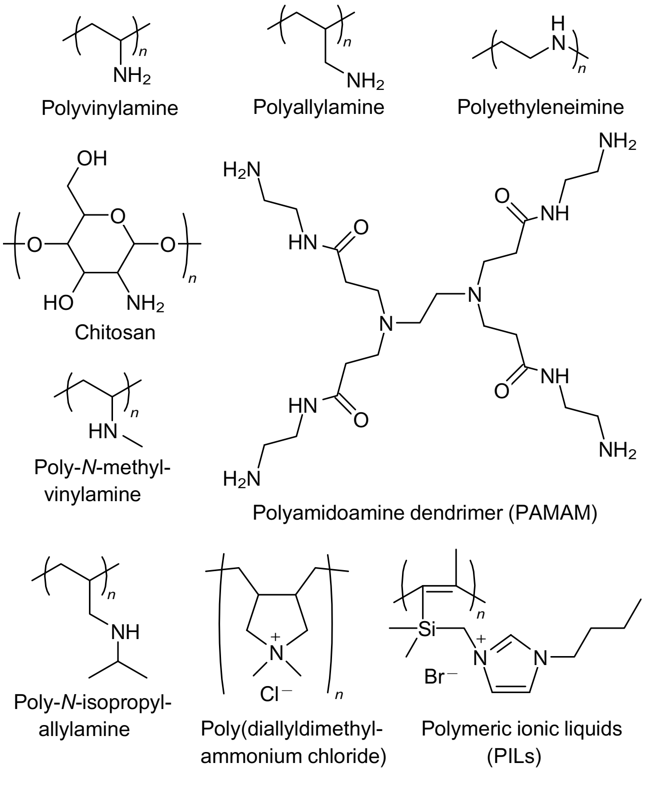


**Figure 13.** Polyamines and polymeric ionic liquids.

An interesting approach is modification of polymers, *e.g.*, poly(ether ether ketones), with polyethyleneimine,[139] although the permeability level observed for polyamines cannot be attained in this way. A considerable drawback of these membranes is the presence of water; this requires moistening of gas streams to preserve the separation properties of the membranes, and the applicability of the membranes is restricted to temperatures not exceeding 100 °C. As a result, such membranes are now used only on a laboratory scale.[150] Meanwhile, the obtained characteristics are suitable for recommending these membranes for fuel cell applications.[151]

A synergistic effect was noted for $CO_2$ reactions with amino groups and quaternary ammonium bases. Indeed, membranes based on vinylamine copolymers with poly(diallyldimethylammonium salts)[148] demonstrating high $CO_2$ permeability (more than 1800 GPU) provide a $CO_2/H_2$ selectivity of about 30 and $CO_2/N_2$ selectivity of about 160. High $CO_2/H_2$ selectivity was found for membranes made of poly(diallyldimethylammonium chloride) doped with low-molecular-weight quaternary ammonium bases:[133] the $CO_2/H_2$ selectivity is about 100 with the $CO_2$ permeability being above 100 GPU.[96, 148]

Polymeric ionic liquids (PILs) with nitrogen-containing cations and various counter-ions are also considered as $CO_2$ transporting materials.[96, 116, 152, 153] The reactions of ionic liquid moieties with $CO_2$, like reactions of other nitrogen-containing groups, is associated with the formation of zwitter-ions or with nucleophilic addition.[152] The selectivity for $CO_2/N_2$ pair attained in composite membranes with PILs can reach 2000, with the permeability exceeding 5000 GPU.[154] However, many PILs, although readily dissolve $CO_2$, still show moderate gas separation characteristics.[96, 135, 138, 153, 155] Nevertheless, some of them reach the upper bound of 2008 for the $CO_2/N_2$ pair.[137, 141] Highly permeable PILs based on polyacetylenes are also close to the 2008 upper bound for $CO_2/N_2$.[156, 157] For PILs, the presence of water in the membrane is not necessary; this forms an advantage for PILs over polyamines and accounts for high practical interest in the synthesis of new PILs.

The specific dipole–quadrupole interactions of $CO_2$ with the membrane material also provide for the ready solubility of $CO_2$ in the polymers.[96, 116] Thermoplastic PEBAX copolymers, that is, block copolymers of PA-6 or PA-12 polyamides with polyethylene oxide or polytetramethylene oxide[96, 116, 158, 159] (see Fig. 1) were among the first materials to demonstrate this effect. It was found that the mobile dipoles of aliphatic polyether units of these polymers can interact with $CO_2$ quadrupoles or with other polar molecules at room temperature.[158] In principle, each dipole can be considered as a specific binding site. The polyether blocks should not be too long, because linear aliphatic polyethers are easily crystallized, which reduces the gas permeability.[159]

The PolyActive membrane developed on the basis of linear copolymers of terephhalic acid polyesters with short poly(ethylene glycol) blocks of various lengths[143] (see Fig. 1) proved to be efficient for the separation of $CO_2$-containing mixtures [up to 50 for $\alpha(CO_2/N_2)$ and up to 8 for $\alpha(CO_2/H_2)$ depending on temperature]. In recent years, the main research efforts in this field have been concentrated on the design of cross-linked aliphatic polyethers,[122, 160] network copolymers of aliphatic polyethers with, for example, polynorbornenes (PNBs) and PDMS[123, 124] and network copolymers with polyethylene glycol and diethylene glycol

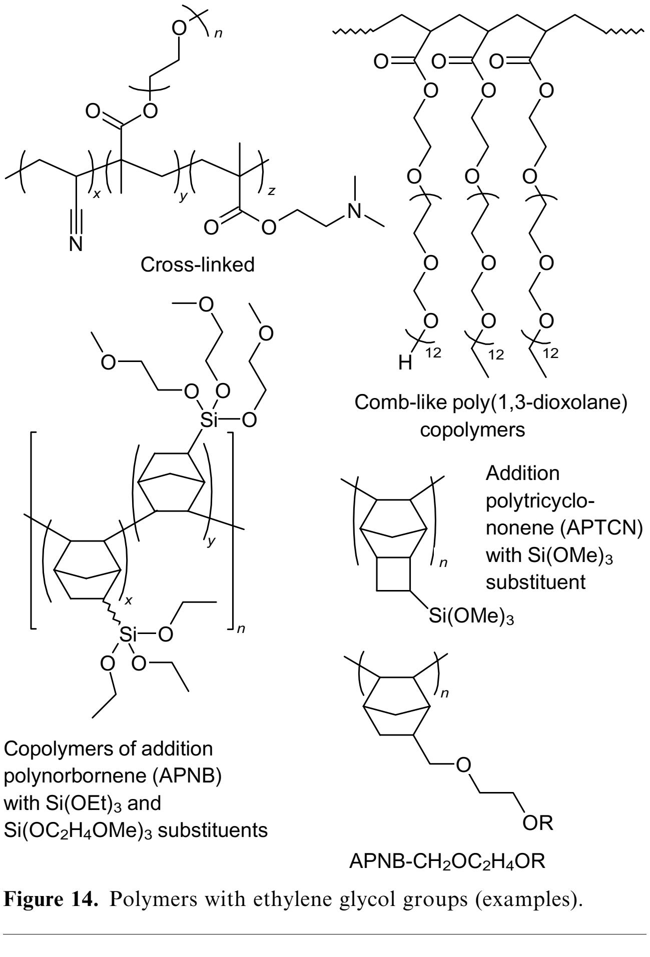


**Figure 14.** Polymers with ethylene glycol groups (examples).

methacrylates,[125,161] particularly those containing nitrogen-containing groups[126,162] (Fig. 14), or polymer matrices filled with ionic liquids.[163,164] Most efficient are comb-like copolymers of poly(1,3-dioxolane)[116,127,129,153] (see Fig. 14), which are located above the upper bounds in the $CO_2/N_2$ and $CO_2/H_2$ plots[127] and, in terms of selectivity values, they are close to the $CO_2$-selective Polaris membranes.[118] Quantum chemical calculations[127] demonstrated that the complex with $CO_2$ is most energetically favourable for these polymers.[116,127,129,153]

The crucial role of the mobility of ether dipoles in the appearance of specific interaction with $CO_2$ is indirectly evidenced by the results of studying glassy polymers with side groups also containing aliphatic ether groups. The introduction of aliphatic ether groups into rigid-chain addition PNBs and polytricyclononenes (PTCNs)[106,128,130,165] (see Fig. 14) also resulted in increasing solubility of $CO_2$, and some of the polymers reach the Robeson upper bound of 2008. However, for rigid-chain polymers, these effects are not as unambiguous as for flexible-chain polymers. For example, upon the successive replacement of the triethoxysilyl side group $Si(OEt)_3$ in additive PNB by $Si(OC_2H_4OMe)_3$ (Refs 128, 165), only the additive PNB-$Si(OC_2H_4OMe)_3$ homopolymer (see Fig. 11) approach the Robeson upper bound for $CO_2/N_2$. In the case of alkoxysilyl-substituted addition PTCNs[106] (see Fig. 11), an increase in the length of the alkyl substituent at the Si–O bond leads only to a decrease in the $CO_2/N_2$ selectivity; meanwhile, the simplest addition PTCN-$Si(OMe)_3$ is located at the upper bound of the Robeson plot for $CO_2/N_2$. Finally, an increase in the length of alkyl group R in the $-CH_2OC_2H_4OR$ side group of addition PNB[130] (see Fig. 14) decreases the selectivity, and only PNB-$CH_2OC_2H_4OMe$ approaches the upper bound. Nevertheless, Alentiev *et al.*[130] estimated the specific interactions by quantum chemical calculations and experimentally by Eqn (13), using separation of the contribution of passive transport for non-interacting gases at low pressures, and demonstrated that these interactions are most pronounced for R = Me.

Thus, analysis of published data indicates that the best characteristics for the separation of $CO_2/N_2$ and $CO_2/H_2$ mixtures are now inherent in polymers capable of specific interactions with $CO_2$; the synthesis and study of these polymers have been recently addressed in numerous publications. PolyActive and Polaris planar composite membranes and pilot units for the isolation of $CO_2$ from gas mixtures were developed on the basis of polymers of this class.

## 8. Conclusion

Thus, despite the fact that each of the indicated separation problems has already been solved either on an industrial scale or on a pilot scale, the gas transport and separation parameters of commercially manufactured membranes are, most often, far from being optimal. This considerably retards the implementation of membrane technologies for solving a variety of problems., *e.g.*, application of membranes for high-temperature separation of hydrogen-containing mixtures or for separation of nitrogen–methane mixtures. The use of membranes not only purifies gas streams from contaminating components that decrease the yield of reaction products, but also solves a variety of environmental problems, for example, reduces the carbon dioxide emission to the atmosphere. In addition, the use of membrane gas separation technologies is relevant if the conventional cryogenic or adsorption techniques cannot be used or are economically unviable. Therefore, it is still necessary to synthesize new polymers and to explore new methods for improving performance of existing membrane materials; this is confirmed by the large number of publications in these fields. The attention is paid to not only the production of materials with high permeability–selectivity characteristics, but also improvement of important parameters such as thermal and chemical stability, structure stability with time, mechanical strength and so on. As demonstrated by the example of PTMSP, research along this line obviously gives beneficial results, for example, it makes it possible to find new efficient ways for increasing the durability of gas separation properties of polymer matrices with retention of the initial level of permeability for chemically diverse polymers. An important role for the prospects of application of a particular new polymer as a membrane material belongs to not only the properties of the material itself, but also the scalability of the synthesis of a new polymer to commercial or pilot production in order to manufacture large-area membranes with stable mechanical characteristics.

The numerous studies related to the application of polymeric materials and gas separation membranes are usually focus either on certain groups of polymers[10–13,31,32,34,35,80,88,89] or on attainment of very important, but specific goals, for example, production of hydrogen[99,111,113] or $CO_2$ recovery and utilization.[102,120–122,154,156,159] Analysis of the broad range of polymers and separation problems in Robeson's studies[8,9] did not consider the possibility of using the accumulated data set for various practical applications of these materials. In the present review, the choice of the most promising materials is based on the correlation approach supplemented by additional analysis of the properties of polymers such as stability of characteristics over time and mechanical properties. The criteria for selection of polymers for gas separation membranes considered in this review do not exhaust the currently existing approaches, but expand their capabilities and thus make the choice more accurate and enable evaluation of not only commercial polymer membranes already existing on the market, but also other both existing and potential polymers and polymer systems. For example, PTMSP stable over time is promising for the production of technical-grade nitrogen from air. A good promise of the recovery of hydrogen from hydrogen-containing mixtures is held by not only highly selective and highly permeable polymers with high ordering of chain packing (triptycene and CANAL polymers), but also thermally stable polymers such as polybenzimidazoles and polynaphthoylbenzimidazoles that can function at temperatures above 200 °C. Perfluorinated and surface-fluorinated polymers are of most interest for the separation of methane-containing mixtures as regards further prospects for the development of membrane technology. The recovery of carbon dioxide from various gas mixtures by polymer membranes is best implemented using polymers capable of specific interactions with $CO_2$ molecules.

The separation of nitrogen–methane mixtures is of special interest for the membrane technology, in particular, for the use of non-porous polymer membranes. Analysis of the literature shows that this problem can be solved using both nitrogen- and methane-selective polymeric materials, depending on the composition of the mixture.

It is important to note that highly permeable and highly selectivity polymers are both of interest, depending on the composition of the initial gas mixture, the required flux and the purity of the final product. Furthermore, the relevant goals include both polymers that can be efficiently applied for solving quite a number of separation problems, for example, the use of membranes with thin selective layers based on polyimides for the separation of air components, recovery of helium from natural gas and separation of biogas components and polymers that are meant for solving specific problems, *e.g.*, the use of thermally stable polymers for the separation of hydrogen-containing mixtures at elevated temperatures.

With obvious necessity and fundamental and practical importance of scientific research in particular fields of polymer synthesis and manufacture of polymer gas separation membranes for solving specific problems, which widely occur in the literature, this integrating review using a number of fundamental approaches made it possible to evaluate various trends of development, prospects and competitiveness of polymer membranes for solving gas separation problems.

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## 9. List of abbreviations and symbols

The following designations are used in the review:

$\alpha$ — permeation selectivity of gases,
$\alpha^D$ — diffusion selectivity of gases,
$\alpha^S$ — solubility selectivity of gases,
$\Delta\alpha$ — deviations of the selectivity values from the upper bound of the permeability – selectivity plots,
$\varepsilon/k$ — effective Lennard – Jones gas – gas interaction potential,
AF2400 — amorphous Teflon AF2400,
$\Delta c$ — gas concentration gradient across the membrane,
$D$ — diffusion coefficient of a gas,
$d$ — effective kinetic diameter of a gas molecule,
$J$ — gas flux through the membrane,
$K_1 - K_4$ — linear correlation parameters for diffusion and solubility coefficients,
$k$ — factor in the Robeson upper bound equation,
$n$ — exponent in the Robeson upper bound equation,
$l$ — thickness of the membrane selective layer,
$Q$ — gas permeability of the membrane,
$P$ — gas permeability coefficient,
$\Delta p$ — pressure drop across the membrane,
$S$ — gas solubility coefficients,
TR — thermally rearranged polymers,
Barrer — gas permeability unit, 1 Barrer = $10^{-10}$ cm$^3$ (STP) cm (cm$^2$ s cm Hg)$^{-1}$,
CA — cellulose acetate,
PAMAM — polyamidoamine dendrimer,
PBI — polybenzimidazole,
PDMS — polydimethylsiloxane,
PEBAX — block copolymers of polyamides with polyethylene oxide,
PHFP — polyhexafluoropropylene,
PILs — polymeric ionic liquids,
PIM-1, PIM-7 — polymers with intrinsic microporosity,
PIs — polyimides,
PNB — polynorbornene,
PNBI — polynaphthoylenebenzimidazole,
PPO — polyphenylene oxide,
PSF — polysulfone,
PTCN — polytricyclononene,
PTMSP — polytrimethylsilylpropyne,
PVTMS — polyvinyltrimethylsilane,
TBPC — tetrabromo-polycarbonate.

## 10. References

1. S.G.Durgar'yan, Y.P.Yampol'skii, N.A.Plate. *Russ. Chem. Rev.*, **57**, 549 (1988)
2. D.R.Paul, Yu.P.Yampol'skii. *Polymeric Gas Separation Membranes*. (Boca Raton, FL: CRC Press, 1994)
3. R.W.Baker, B.T.Low. *Macromolecules*, **47**, 6999 (2014)
4. A.F.Ismail, K.Chandra Khulbe, T.Matsuura. *Gas Separation Membranes: Polymeric and Inorganic*. (1st Edn). (Cham: Springer, Imprint, 2015)
5. M.Galizia, W.S.Chi, Z.P.Smith, T.C.Merkel, R.W.Baker, B.D.Freeman. *Macromolecules*, **50**, 7809 (2017)
6. S.Matteucci, Y.Yampolskii, B.D.Freeman, I.Pinnau. In *Materials Science of Membranes for Gas and Vapor Separation*. (Eds Y.Yampolskii, I.Pinnau, B.Freeman). (Chichester, UK: Wiley, 2006). P. 1
7. L.McKeen. *Permeability Properties of Plastics and Elastomers*. (4th Edn). (Amsterdam, Boston: Elsevier William Andrew, 2017)
8. L.M.Robeson. *J. Membr. Sci.*, **62**, 165 (1991)
9. L.M.Robeson. *J. Membr. Sci.*, **320**, 390 (2008)
10. R.Swaidan, B.Ghanem, I.Pinnau. *ACS Macro Lett.*, **4**, 947 (2015)
11. A.X.Wu, J.A.Drayton, Z.P.Smith. *AIChE J.*, **65**, e16700 (2019)
12. B.Comesaña-Gándara, J.Chen, C.G.Bezzu, M.Carta, I.Rose, M.-C.Ferrari, E.Esposito, A.Fuoco, J.C.Jansen, N.B.McKeown. *Energy Environ. Sci.*, **12**, 2733 (2019)
13. W.H.Lee, J.G.Seong, X.Hu, Y.M.Lee. *J. Polym. Sci.*, **58**, 2450 (2020)
14. A.Alentiev, Y.Yampolskii. *Ind. Eng. Chem. Res.*, **52**, 8864 (2013)
15. Database 'Polymer Gas Separation Membranes', Membrane Society of Australasia; https://www.membrane-australasia.org/polymer-gas-separation-membranes/
16. Polymer Database 'PoLyInfo', National Institute for Materials Science (NIMS); https://polymer.nims.go.jp/en/
17. Baza Dannykh 'Gazorazdelitel'nye Parametry Stekloobraznykh Polimerov', Informregistr RF, 3585, INKHS RAN, 1998 (Database 'Gas Separation Parameters of Glassy Polymers', Informregister RF, 3585, Institute of Petrochemical Synthesis, RAS, 1998)
18. V.V.Teplyakov, S.G.Durgaryan. *Vysokomol. Soedin. A*, **26**, 1498 (1984)
19. V.Teplyakov, P.Meares. *Gas Separation & Purification*, **4**, 66 (1990)
20. M.Yáñez, A.Ortiz, D.Gorri, I.Ortiz. *Int. J. Hydrogen Energy*, **46**, 17507 (2021)
21. Y.Wang, X.Ma, B.S.Ghanem, F.Alghunaimi, I.Pinnau, Y.Han. *Mater. Today Nano*, **3**, 69 (2018)
22. M.Bozorg, B.Addis, V.Piccialli, Á.A.Ramírez-Santos, C.Castel, I.Pinnau, E.Favre. *Chem. Eng. Sci.*, **207**, 1196 (2019)
23. D.S.Karousos, E.P.Favvas. *Int. J. Membrane Sci. Technol.*, **9**, 14 (2022)
24. S.Y.Yoon, B.S.Choi, J.H.Ahn, T.S.Kim. *Appl. Thermal Eng.*, **151**, 163 (2019)
25. K.Chong, S.-O.Lai, H.S.Thiam, H.C.Teoh, S.Heng. *JESTEC*, **11**, 1016 (2016)
26. W.Zhang, S.Huang, S.Wu, Y.Wu, J.Gao. *Fuel*, **254**, 115699 (2019)
27. Y.Alqaheem, F.Alswaileh. *Membranes*, **11**, 211 (2021)
28. N.F.Himma, A.K.Wardani, N.Prasetya, P.T.P.Aryanti, I.G.Wenten. *Rev. Chem. Eng.*, **35**, 591 (2019)
29. B.Adhikari, C.J.Orme, J.R.Klaehn, F.F.Stewart. *Separation and Purification Technology*, **268**, 118703 (2021)

30. S.Haider, A.Lindbråthen, J.A.Lie, M.-B.Hägg. *Separation and Purification Technology*, **205**, 251 (2018)
31. Z.-X.Low, P.M.Budd, N.B.McKeown, D.A.Patterson. *Chem. Rev.*, **118**, 5871 (2018)
32. A.Yu.Alent'ev, V.E.Ryzhikh, N.A.Belov. *Polym. Sci. Ser. C*, **62**, 238 (2020)
33. S.M.Meckler, J.E.Bachman, B.P.Robertson, C.Zhu, J.R.Long, B.A.Helms. *Angew. Chem., Int. Ed.*, **57**, 4912 (2018)
34. S.Banerjee, D.Bera. In *Membrane Materials for Gas and Vapor Separation*. (Eds Y.Yampolskii, E.Finkelshtein). (Chichester, UK: Wiley, 2017). P. 223
35. Barnali Dasgupta Ghosh, Susanta Banerjee, Alexander Alentiev, Inga Ronova, Yuri Yampolskii. In *Imidic Polymers and Green Polymer Chemistry. New Technology and Developments in Process and Product*. (Eds A.I.Barzic, N.K.Rawat, A.K.Haghi). (Palm Bay, FL: Apple Academic Press, 2021). P. 23
36. B.S.Ghanem, F.Alghunaimi, Y.Wang, G.Genduso, I.Pinnau. *ACS Omega*, **3**, 11874 (2018)
37. A.Yerzhankyzy, B.S.Ghanem, Y.Wang, N.Alaslai, I.Pinnau. *J. Membr. Sci.*, **595**, 117512 (2020)
38. A.A.Shamsabadi, F.Seidi, M.Nozari, M.Soroush. *ChemSusChem*, **11**, 472 (2018)
39. B.B.Shrestha, K.Wakimoto, Z. Wang, A.P.Isfahani, T.Suma, E.Sivaniah, B.Ghalei. *RSC Adv.*, **8**, 6326 (2018)
40. K.Halder, P.Georgopanos, S.Shishatskiy, V.Filiz, V.Abetz. *J. Polym. Sci. Part A: Polym. Chem.*, **56**, 2752 (2018)
41. C.G.Bezzu, M.Carta, M.-C.Ferrari, J.C.Jansen, M.Monteleone, E.Esposito, A.Fuoco, K.Hart, T.P.Liyana-Arachchi, C.M.Colina, N.B.McKeown. *J. Mater. Chem. A*, **6**, 10507 (2018)
42. I.Hossain, A.Al Munsur, T.-H.Kim. *Membranes*, **9**, 113 (2019)
43. A.Fuoco, B.Satilmis, T.Uyar, M.Monteleone, E.Esposito, C.Muzzi, E.Tocci, M.Longo, M.P.De Santo, M.Lanč, K.Friess, O.Vopička, P.Izák, J.C.Jansen. *J. Membr. Sci.*, **594**, 117460 (2020)
44. I.Hossain, A.Husna, D.Kim, T.-H.Kim. *Membr. J.*, **30**, 420 (2020)
45. X.Han, J.Zhang, C.Yue, J.Pang, H.Zhang, Z.Jiang. *J. Industr. Eng. Chem.*, **91**, 102 (2020)
46. Z.Zhu, H.Dong, K.Li, Q.Li, J.Li, X.Ma. *Separation and Purification Technology*, **262**, 118313 (2021)
47. E.Caliskan, S.Shishatskiy, S.Neumann, V.Abetz, V.Filiz. *Polymers*, **14**, 119 (2021)
48. L.Starannikova, N.Belov, V.Shantarovich, J.Zhang, J.Jin, Y.Yampolskii. *J. Membr. Sci.*, **548**, 593 (2018)
49. X.Hu, Y.He, Z.Wang, J.Yan. *Polymer*, **153**, 173 (2018)
50. X.Xu, J.Wang, J.Dong, H.-B.Li, Q.Zhang, X.Zhao. *J. Membr. Sci.*, **602**, 117967 (2020)
51. X.Hu, W.H.Lee, J.Y.Bae, J. Zhao, J.S.Kim, Z.Wang, J. Yan, Y.M.Lee. *J. Membr. Sci.*, **615**, 118533 (2020)
52. M.A.Abdulhamid, H.W.H.Lai, Y.Wang, Z.Jin, Y.C.Teo, X.Ma, I.Pinnau, Y.Xia. *Chem. Mater.*, **31**, 1767 (2019)
53. B.Díez, P.Cuadrado, Á. Marcos-Fernández, J.G.de la Campa, A.Tena, P.Prádanos, L.Palacio, Y.M.Lee, C.Alvarez, Á.E.Lozano, A.Hernández. *Reactive and Functional Polymers*, **127**, 38 (2018)
54. J.Lee, J.S.Kim, J.F.Kim, H.J.Jo, H.Park, J.G.Seong, Y.M.Lee. *J. Membr. Sci.*, **573**, 393 (2019)
55. S.Luo, Q.Zhang, T.K.Bear, T.E.Curtis, R.K.Roeder, C.M.Doherty, A.J.Hill, R.Guo. *J. Membr. Sci.*, **551**, 305 (2018)
56. M.S.AlQahtani, K.Mezghani. *J. Nat. Gas Sci. Eng.*, **51**, 262 (2018)
57. L.Ye, L.Wang, X.Jie, C.Yu, G.Kang, Y.Cao. *J. Membr. Sci.*, **573**, 21 (2019)
58. D.Meis, A.Tena, S.Neumann, P.Georgopanos, T.Emmler, S.Shishatskiy, S.Rangou, V.Filiz, V.Abetz. *Polym. Chem.*, **9**, 3987 (2018)
59. X.Jiang, X.Xiao, J. Dong, X.Xu, X.Zhao, Q.Zhang. *J. Membr. Sci.*, **564**, 605 (2018)
60. J.S.Kim, S.J. Moon, H.H.Wang, S.Kim, Y.M.Lee. *J. Membr. Sci.*, **582**, 381 (2019)
61. C.Aguilar-Lugo, C.Álvarez, Y.M.Lee, J.G.de la Campa, Á.E.Lozano. *Macromolecules*, **51**, 1605 (2018)
62. X.Hu, W.H.Lee, J.Y.Bae, J.S.Kim, J.T.Jung, H.H.Wang, H.J.Park, Y.M.Lee. *J. Membr. Sci.*, **612**, 118437 (2020)
63. S.Luo, Q.Zhang, L.Zhu, H.Lin, B.A.Kazanowska, C.M.Doherty, A.J. Hill, P.Gao, R.Guo. *Chem. Mater.*, **30**, 5322 (2018)
64. X.Ma, H.W.H.Lai, Y.Wang, A.Alhazmi, Y.Xia, I.Pinnau. *ACS Macro Lett.*, **9**, 680 (2020)
65. H.W.H.Lai, F.M.Benedetti, J.M.Ahn, A.M.Robinson, Y.Wang, I.Pinnau, Z.P.Smith, Y.Xia. *Science*, **375**, 1390 (2022)
66. I.I.Ponomarev, Y.A.Volkova, I.I.Ponomarev, D.Y.Razorenov, K.M.Skupov, R.Y.Nikiforov, S.V.Chirkov, V.E.Ryzhikh, N.A.Belov, A.Y.Alentiev. *Polymer*, **238**, 124396 (2022)
67. N.Muruganandam, D.R.Paul. *J. Membr. Sci.*, **34**, 185 (1987)
68. C.T.Wright, D.R.Paul. *J. Appl. Polym. Sci.*, **67**, 875 (1998)
69. S.Escorihuela, A.Tena, S.Shishatskiy, S.Escolástico, T.Brinkmann, J. Serra, V.Abetz. *Membranes*, **8**, 16 (2018)
70. J. Hao, K.Tanaka, H.Kita, K.-I.Okamoto. *J. Polym. Sci. A Polym. Chem.*, **36**, 485 (1998)
71. A.Yu.Alentiev, Yu.P.Yampolskii, V.P.Shantarovich, S.M.Nemser, N.A.Platé. *J. Membr. Sci.*, **126**, 123 (1997)
72. J.S.McHattie, W.J. Koros, D.R.Paul. *Polymer*, **32**, 840 (1991)
73. A.Yu.Alentiev, N.A.Belov, S.V.Chirkov, Yu.P.Yampolskii. *J.Membr. Sci.*, **547**, 99 (2018)
74. Y.P.Yampol'skii, E.Sh.Finkelshtein. *Membrane Materials for Gas and Vapor Separation: Synthesis and Application of Silocon-Containing Polymers*. John Wiley & Sons, Inc, Chichester, West Sussex, United Kingdom, 2017
75. S.M.Matson, A.A.Kossov, V.P.Makrushin, I.S.Levin, N.A.Zhilyaeva, E.G.Litvinova, V.S.Khotimskiy. *Polym. Sci. Ser. C*, **61**, 76 (2019)
76. S.M.Matson, V.P.Makrushin, I.S.Levin, E.G.Litvinova, V.S.Khotimskiy. *Membr. Membr. Technol.*, **2**, 383 (2020)
77. S.Shishatskiy, V.Makrushin, I.Levin, P.Merten, S.Matson, V.Khotimskiy. *Polymers*, **14**, 462 (2022)
78. I.I.Ponomarev, D.Yu.Razorenov, I.V.Blagodatskikh, A.V.Muranov, L.E.Starannikova, A.Yu.Alent'ev, R.Yu.Nikiforov, Yu.P.Yampol'skii. *Polym. Sci. Ser. B*, **61**, 605 (2019)
79. I.I.Ponomarev, K.M.Skupov, K.A.Lyssenko, I.V.Blagodatskikh, A.V.Muranov, Y.A.Volkova, D.Yu.Razorenov, I.I.Ponomarev, L.E.Starannikova, D.A.Bezgin, A.Yu. Alentiev, Y.P.Yampolskii. *Mendeleev Commun.*, **30**, 734 (2020)
80. M.A.Gulyanskii, A.A.Kotenko, E.G.Krasheninnikov, M.E.Kuz'menko, S.V.Potekhin, A.A.Fedotov. In *Membrany-2022. XV Yubileinaya Vserossiiskaya Nauchnaya Konferentsiya (s Mezhdunarodnym Uchastiem). Tezisy Dokladov. (Membranes-2022. The XXnd Anniversary All-Russian Scientific Conference (with International Participation). Abstracts.* (Russian University of Chemical Technology named after D.I. Mendeleev, Tula Region, 2022). P. 146
81. W.L.Robb. *Annals of the New York Academy of Sciences*, **146**, 119 (1968)
82. Yu.Yampolskii, N.Belov, A.Alentiev. *J. Membr. Sci.*, **598**, 117779 (2020)
83. Y.P.Yampolskii, N.A.Belov, A.Yu.Alentiev. *Russ. Chem. Rev.*, **88**, 387 (2019)
84. N.Belov, R.Nikiforov, E.Polunin, Yu.Pogodina, I.Zavarzin, V.Shantarovich, Yu.Yampolskii. *J. Membr. Sci.*, **565**, 112 (2018)
85. R.Nikiforov, N.Belov, A.Zharov, I.Konovalova, B.Shklyaruk, Yu. Yampolskii. *J. Membr. Sci.*, **540**, 129 (2017)
86. N.A.Belov, D.S.Pashkevich, A.Y.Alentiev, A.Tressaud. *Membranes*, **11**, 713 (2021)

87. N.A.Belov, A.Yu.Alentiev, R.Yu.Nikiforov, S.V.Chirkov, D.A.Bezgin, D.A.Syrtsova, V.E.Ryzhikh, I.I.Ponomarev. *Polymers*, in press (2022)
88. X.Ma, K.Li, Z.Zhu, H.Dong, J.Lv, Y.Wang, I.Pinnau, J.Li, B.Chen, Y.Han. *J. Mater. Chem. A*, **9**, 18313 (2021)
89. M.Fang, Z.He, T.C.Merkel, Y.Okamoto. *J. Mater. Chem. A*, **6**, 652 (2018)
90. M.Yavari, M.Fang, H.Nguyen, T.C.Merkel, H.Lin, Y.Okamoto. *Macromolecules*, **51**, 2489 (2018)
91. M.A.El-Okazy, L.Liu, C.P.Junk, E.Kathmann, W.White, S.E.Kentish. *J. Membr. Sci.*, **634**, 119401 (2021)
92. Y.Okamoto, H.-C.Chiang, M.Fang, M.Galizia, T.Merkel, M.Yavari, H.Nguyen, H.Lin. *Membranes*, **10**, 394 (2020)
93. N.W.Ockwig, T.M.Nenoff. *Chem. Rev.*, **107**, 4078 (2007)
94. Y.He, F.M.Benedetti, S.Lin, C.Liu, Y.Zhao, H.Ye, T.Van Voorhis, M.G.De Angelis, T.M.Swager, Z.P.Smith. *Adv. Mater.*, **31**, 1807871 (2019)
95. A.Yu.Alent'ev, Yu.P.Yampolskii, M.N.Vidyakin, Yu.N.Lazareva. *Polym. Sci. Ser. A*, **48**, 1120 (2006)
96. A.Yu.Alentiev, V.E.Ryzhikh, N.A.Belov. *Polym. Sci. Ser. C*, **63**, 181 (2021)
97. S.M.Matson, E.G.Litvinova, V.K.Chernikov, G.N.Bondarenko, V.S.Khotimskiy. *Polymer*, **236**, 124308 (2021)
98. G.O.Karpov, D.S.Bakhtin, M.V.Bermeshev, I.L.Borisov, B.A.Bulgakov, V.V.Volkov, E.Sh. Finkelstein. *Polym. Sci. Ser. B*, **61**, 387 (2019)
99. G.O.Karpov, M.V.Bermeshev, I.L.Borisov, S.R.Sterlin, A.A.Tyutyunov, N.P.Yevlampieva, B.A.Bulgakov, V.V.Volkov, E.S.Finkelshtein. *Polymer*, **153**, 626 (2018)
100. G.O.Karpov, I.L.Borisov, A.V.Volkov, E.Sh.Finkelshtein, M.V.Bermeshev. *Polymers*, **12**, 1282 (2020)
101. E.V.Bermesheva, A.I.Wozniak, I.L.Borisov, N.P.Yevlampieva, O.S.Vezo, G.O.Karpov, M.V.Bermeshev, A.F.Asachenko, M.A.Topchiy, P.S.Gribanov, M.S.Nechaev, V.V.Volkov, E.Sh.Finkelshtein. *Polym. Sci. Ser. C*, **61**, 86 (2019)
102. W.Dujardin, C.Van Goethem, J.A.Steele, M.Roeffaers, I.F.J.Vankelecom, G.Koeckelberghs. *Polymers*, **11**, 704 (2019)
103. A.A.Morontsev, V.A.Zhigarev, R.Y.Nikiforov, N.A.Belov, M.L.Gringolts, E.S.Finkelshtein, Y.P.Yampolskii. *Eur. Polym. J.*, **99**, 340 (2018)
104. A.I.Wozniak, E.V.Bermesheva, I.L.Borisov, D.I.Petukhov, M.V.Bermeshev, A.V.Volkov, E.Sh.Finkelshtein. *Macromol. Rapid Commun.*, **40**, 1900206 (2019)
105. A.I.Wozniak, E.V.Bermesheva, F.A.Andreyanov, I.L.Borisov, D.P.Zarezin, D.S.Bakhtin, N.N.Gavrilova, I.R.Ilyasov, M.S.Nechaev, A.F.Asachenko, M.A.Topchiy, A.V.Volkov, E.Sh.Finkelshtein, X.-K.Ren, M.V.Bermeshev. *React. Funct. Polym.*, **149**, 104513 (2020)
106. D.A.Alentiev, E.S.Egorova, M.V.Bermeshev, L.E.Starannikova, M.A.Topchiy, A.F.Asachenko, P.S.Gribanov, M.S.Nechaev, Y.P.Yampolskii, E.Sh.Finkelshtein. *J. Mater. Chem. A*, **6**, 19393 (2018)
107. L.Hu, S.Pal, H.Nguyen, V.Bui, H.Lin. *J. Polym. Sci.*, **58**, 2467 (2020)
108. A.T.Pingitore, M.Molleo, T.J.Schmidt, B.C.Benicewicz. In *Encyclopedia of Sustainability Science and Technology*. (Ed. R.A.Meyers). (New York, NY: Springer, 2018). P. 1
109. K.A.Stevens, J.D.Moon, H.Borjigin, R.Liu, R.M.Joseph, J.S.Riffle, B.D.Freeman. *J. Membr. Sci.*, **593**, 117427 (2020)
110. L.Zhu, M.T.Swihart, H.Lin. *Energy Environ. Sci.*, **11**, 94 (2018)
111. A.Naderi, A.Asadi Tashvigh, T.-S.Chung. *J. Membr. Sci.*, **572**, 343 (2019)
112. X.Wang, M.Shan, X.Liu, M.Wang, C.M.Doherty, D.Osadchii, F.Kapteijn. *ACS Appl. Mater. Interfaces*, **11**, 20098 (2019)
113. J.D.Moon, A.T.Bridge, C.D Ambra, B.D.Freeman, D.R.Paul. *J. Membr. Sci.*, **582**, 182 (2019)
114. T.C.Merkel, M.Zhou, R.W.Baker. *J. Membr. Sci.*, **389**, 441 (2012)
115. A.Yu.Alent'ev, A.V.Volkov, I.V.Vorotyntsev, A.L.Maksimov, A.B.Yaroslavtsev. *Membr. Membr. Technol.*, **3**, 255 (2021)
116. Y.Han, W.S.W.Ho. *J. Membr. Sci.*, **628**, 119244 (2021)
117. Y.Han, W.S.W.Ho. *J. Polym. Sci.*, **58**, 2435 (2020)
118. V.Batoon, A.Borsaly, C.Casillas, T.Hofmann, I.Huang, J.Kniep, T.Merkel, C.Paulaha, W.Salim, E.Westling. *SSRN J.*, (2022)
119. L.Zhu, M.T.Swihart, H.Lin. *Energy & Environmental Science*, **11**, 94 (2018)
120. K.A.Lokhandwala, I.Pinnau, Z.He, K.D.Amo, A.R.DaCosta, J.G.Wijmans, R.W.Baker. *J. Membr. Sci.*, **346**, 270 (2010)
121. S.Shishatskiy, C.Nistor, M.Popa, S.P.Nunes, K.V.Peinemann. *Adv. Eng. Mater.*, **8**, 390 (2006)
122. L.Huang, J.Liu, H.Lin. *J. Membr. Sci.*, **610**, 118253 (2020)
123. I.Hossain, D.Kim, A.Z.Al Munsur, J.M.Roh, H.B.Park, T.-H.Kim. *ACS Appl. Mater. Interfaces*, **12**, 27286 (2020)
124. D.Kim, I.Hossain, Y.Kim, O.Choi, T.-H.Kim. *Polymers*, **12**, 1674 (2020)
125. C.-Y.Park, B.-J. Chang, J.-H.Kim, Y.M.Lee. *J. Membr. Sci.*, **587**, 117167 (2019)
126. J.Deng, Z.Dai, J.Yan, M.Sandru, E.Sandru, R.J. Spontak, L.Deng. *J. Membr. Sci.*, **570–571**, 455 (2019)
127. J.Liu, S.Zhang, D.Jiang, C.M.Doherty, A.J. Hill, C.Cheng, H.B.Park, H.Lin. *Joule*, **3**, 1881 (2019)
128. C.R.Maroon, J.Townsend, M.A.Higgins, D.J. Harrigan, B.J.Sundell, J.A.Lawrence, J.T.O Brien, D.O Neal, K.D.Vogiatzis, B.K.Long. *J. Membr. Sci.*, **595**, 117532 (2020)
129. J. Liu, G.Zhang, K.Clark, H.Lin. *ACS Appl. Mater. Interfaces*, **11**, 10933 (2019)
130. D.A.Alentiev, R.Yu.Nikiforov, M.A.Rudakova, D.P.Zarezin, M.A.Topchiy, A.F.Asachenko, A.Yu.Alentiev, B.D.Bolshchikov, N.A.Belov, E.Sh. Finkelshtein, M.V.Bermeshev. *J. Membr. Sci.*, **648**, 120340 (2022)
131. A.I.Wozniak, E.V.Bermesheva, I.L.Borisov, A.V.Volkov, D.I.Petukhov, N.N.Gavrilova, V.P.Shantarovich, A.F.Asachenko, M.A.Topchiy, E.S.Finkelshtein, M.V.Bermeshev. *J. Membr. Sci.*, **641**, 119848 (2022)
132. T.-J.Kim, H.Vraalstad, M.Sandru, M.-B.Hägg. *J. Membr. Sci.*, **428**, 218 (2013)
133. K.K.Chen, W.Salim, Y.Han, M.Gasda, W.S.W.Ho. *J. Membr. Sci.*, **612**, 118484 (2020)
134. L.Ye, L.Wan, J. Tang, Y.Li, F.Huang. *RSC Adv.*, **8**, 8552 (2018)
135. J.Yin, C.Zhang, Y.Yu, T.Hao, H.Wang, X.Ding, J.Meng. *J. Membr. Sci.*, **593**, 117405 (2020)
136. H.You, I.Hossain, T.-H.Kim. *RSC Adv.*, **8**, 1328 (2018)
137. L.C.Tomé, D.C.Guerreiro, R.M.Teodoro, V.D.Alves, I.M.Marrucho. *J. Membr. Sci.*, **549**, 267 (2018)
138. A.Ito, T.Yasuda, T.Yoshioka, A.Yoshida, X.Li, K.Hashimoto, K.Nagai, M.Shibayama, M.Watanabe. *Macromolecules*, **51**, 7112 (2018)
139. Y.Yu, J.Wang, Y.Wang, W.Pan, C.Liu, P.Liu, L.Liang, C.Xu, Y.Liu. *J. Ind. Eng. Chem.*, **83**, 20 (2020)
140. C.Wang, F.Guo, H.Li, J. Xu, J. Hu, H.Liu, M.Wang. *J. Membr. Sci.*, **598**, 117677 (2020)
141. R.M.Teodoro, L.C.Tomé, D.Mantione, D.Mecerreyes, I.M.Marrucho. *J. Membr. Sci.*, **552**, 341 (2018)
142. J.Li, S.Wang, K.Nagai, T.Nakagawa, A.W.-H.Mau. *J. Membr. Sci.*, **138**, 143 (1998)
143. Md.M.Rahman, C.Abetz, S.Shishatskiy, J.Martin, A.J.Müller, V.Abetz. *ACS Appl. Mater. Interfaces*, **10**, 26733 (2018)
144. R.Rea, M.De Angelis, M.Baschetti. *Membranes*, **9**, 26 (2019)
145. X.Deng, C.Zou, Y.Han, L.-C.Lin, W.S.W.Ho. *J. Phys. Chem. C*, **124**, 25322 (2020)
146. S.Dong, Z.Wang, M.Sheng, Z.Qiao, J. Wang. *J. Membr. Sci.*, **610**, 118221 (2020)

147. B.Belaissaoui, E.Lasseuguette, S.Janakiram, L.Deng, M.-C.Ferrari. *Membranes*, **10**, 367 (2020)
148. Y.Han, W.S.W.Ho. *Chin. J. Chem. Eng.*, **26**, 2238 (2018)
149. Z.Tong, W.S.W.Ho. *J. Membr. Sci.*, **543**, 202 (2017)
150. Y.Han, D.Wu, W.S.W.Ho. *J. Membr. Sci.*, **573**, 476 (2019)
151. W.Salim, Y.Han, V.Vakharia, D.Wu, D.J. Wheeler, W.S.W.Ho. *J. Membr. Sci.*, **573**, 465 (2019)
152. A.Klemm, Y.-Y.Lee, H.Mao, B.Gurkan. *Front. Chem.*, **8**, 637 (2020)
153. Y.Han, W.S.W.Ho. *J. Polym. Eng.*, **40**, 529 (2020)
154. E.Kamio, M.Tanaka, Y.Shirono, Y.Keun, F.Moghadam, T.Yoshioka, K.Nakagawa, H.Matsuyama. *Ind. Eng. Chem. Res.*, **59**, 2083 (2020)
155. I.Kammakakam, K.E.O Harra, J.E.Bara, E.M.Jackson. *ACS Omega*, **4**, 3439 (2019)
156. V.Polevaya, V.Geiger, G.Bondarenko, S.Shishatskiy, V.Khotimskiy. *Materials*, **12**, 2763 (2019)
157. V.Polevaya, A.Vorobei, A.Gavrikov, S.Matson, O.Parenago, S.Shishatskiy, V.Khotimskiy. *Polymers*, **12**, 2468 (2020)
158. Q.Trong Nguyen, J. Sublet, D.Langevin, C.Chappey, S.Marais, J.-M.Valleton, F.Poncin-Epaillard. In *Membrane Gas Separation*. (Eds Y.Yampolskii, B.Freeman). John Wiley & Sons, Ltd, Chichester, UK, 2010. P. 255
159. A.Car, C.Stropnik, W.Yave, K.-V.Peinemann. *Adv. Funct. Mater.*, **18**, 2815 (2008)
160. G.K.Kline, J.R.Weidman, Q.Zhang, R.Guo. *J. Membr. Sci.*, **544**, 25 (2017)
161. F.H.Akhtar, M.Kumar, H.Vovusha, R.Shevate, L.F.Villalobos, U.Schwingenschlögl, K.-V.Peinemann. *Macromolecules*, **52**, 6213 (2019)
162. S.Li, X.Jiang, X.Yang, Y.Bai, L.Shao. *J. Membr. Sci.*, **570**–**571**, 278 (2019)
163. J.Deng, J.Yu, Z.Dai, L.Deng. *Ind. Eng. Chem. Res.*, **58**, 5261 (2019)
164. V.A.Kusuma, C.Chen, J.S.Baker, M.K.Macala, D.Hopkinson. *Polymer*, **180**, 121666 (2019)
165. C.R.Maroon, J.Townsend, K.R.Gmernicki, D.J.Harrigan, B.J.Sundell, J.A.Lawrence, S.M.Mahurin, K.D.Vogiatzis, B.K.Long. *Macromolecules*, **52**, 1589 (2019)