DOI: 10.1070/RCR4861

# Fluorine in the structure of polymers: influence on the gas separation properties

**Yuri P. Yampolskii, Nikolay A. Belov, Alexandre Yu. Alentiev**

*A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences*
*Leninsky prosp. 29, 119991 Moscow, Russian Federation*

Results of studies on the separation of gases and vapours using fluorine-containing polymers are integrated and analyzed. Methods for the synthesis of these polymers are considered, including direct gas-phase fluorination, plasma polymerization of fluorine-containing precursors and modification of organic polymers, as well as diverse syntheses of monomers containing C – F and C – $CF_3$ bonds and their subsequent polymerization. Structure – property relationships for these polymers are elucidated and their actual and potential applications as membrane materials are discussed.
The bibliography includes 165 references.

## Contents

1. Introduction 387
2. Membrane gas separation principles 388
3. Direct gas-phase fluorination of polymers 389
4. Plasma chemical treatment of polymers 390
5. Effect of fluorine-containing groups on the gas transport properties of amorphous polymers 391
6. Industrial fluorine-containing polymers 401
7. Conclusion 402

## 1. Introduction

The chemistry of organic fluorine compounds is an extensive and important part of modern organic chemistry.[1] These compounds are especially significant for medicinal chemistry and pharmaceutics. Suffice it to say that 25% of all modern pharmaceutical drugs are based on fluorine compounds.[2] The very strong C – F bond present in an organic molecule imparts unique properties to the molecule. The fluorine atom is highly electronegative. Many organofluorine compounds are volatile; therefore, they started to be used as working fluids in refrigerators. Even such compound as $UF_6$ is highly volatile, which accounts for its use for uranium isotope enrichment. The application of initially very popular chlorofluorocarbons was prohibited by the Montreal Protocol, because of their detrimental effect on the ozone layer of the Earth. Currently, these compounds have been successfully replaced by fluorocarbons, which, however, behave as greenhouse gases. Bromofluorocarbons are known as fire-extinguishing and fire-protective means (for example, they are used to treat workwear fabrics). In medicine, fluorinated compounds are used not only for drug production, but also as volatile anaesthetic fluids and blood substitutes (perfluorane). Compounds labelled with the $^{18}F$ isotope, which decays to give off positrons, are employed for computer tomography. Other applications of organofluorine compounds are also known, *e.g.*, for surface hydrophobization, textile treatment and preparation of surfactants.

Fluorine-containing polymers are of particular value. The number of fluorinated monomers able to undergo polymerization or polycondensation reactions is far less than the number of common organic monomers; nevertheless, the structures and properties of fluoropolymers are fairly diverse.[3 – 8] By far not all of them have high molecular weight and exhibit film-forming properties needed to fabricate membrane materials. The synthesis of fluorine-containing polymers was usually conducted to reach the desired optical or electrical properties (for the application as photoresists, litographic materials, optical waveguides and so on). However, in many cases, the studies on the synthesis and properties of fluorine-containing polymers are related particularly to the possible application of these polymers as gas separation membrane materials.

**Yu.P.Yampolskii**. Doctor of Science (Chemistry), Professor, Chief Researcher at the TIPS RAS.
Telephone: +7(495)647 – 5927 (ext. 210), e-mail: Yampol@ips.ac.ru
**N.A.Belov**. Candidate of Science (Chemistry), Senior Researcher at the TIPS RAS.
Telephone: +7(495)647 – 5927 (ext. 210), e-mail: belov@ips.ac.ru
**A.Yu.Alentiev**. Doctor of Science (Chemistry), Professor, Leading Researcher at the TIPS RAS.
Telephone: +7(495)647 – 5927 (ext. 210), e-mail: Alentiev@ips.ac.ru
**Current research interests of the authors**: membranes, gas permeation, diffusion, chemical thermodynamics, silicon-containing polymers, perfluorinated polymers, membrane materials science.

Received 4 October 2018
Translation: Z.P.Svitanko

© 2019 Uspekhi Khimii, Russian Academy of Sciences and Turpion Ltd.

Currently, published reviews are available on the preparation of fluorine-containing polymers with complete or sporadic description of their properties [3, 6] and on the use of industrial fluorinated polymers.[4, 5, 9] There are also reviews covering the membrane properties of particular classes of macromolecular fluorine compounds, condensation polymers (polyarylenes, polyamides, polyimides, polyphosphazenes and so on),[3] norbornene polymers,[10] polyacetylenes,[11] perfluorinated polymers,[12] and reviews briefly considering the transport properties of these polymers.[13] However, none of the publications give systematic survey and analysis of the transport properties of polymers with related structures either fluorinated or not, which is important for establishing the relationship between the structure and properties of membrane materials as the base of targeted search for compounds with better properties.

The present review addresses fluorine-containing polymers with different structures including their membrane properties and methods for their synthesis such as direct gas-phase fluorination and plasma treatment of polymers. The effect of introduction of $CF_3$ groups and fluorine atoms into amorphous glassy polymers of various classes (polystyrenes, polyimides, polyamides, polyacetylenes, polynorbornenes, *etc.*) is discussed. The attention is focused on the effect of the structure of amorphous fluorine-containing glassy polymers on parameters such as gas permeability and separation factor and free volume of the materials.

The following abbreviations are used:

α — selectivity, separation factor,

AN — acrylonitrile,

BPDA — 3,3′,4,4′-biphenyltetracarboxylic dianhydride,

BTDA — 3,3′,4,4′-benzophenonetetracarboxylic dianhydride,

$D$ — gas diffusion coefficient,

$D_i$ — concentration-averaged gas diffusion coefficient,

6FDA — 4,4′-(hexafluoroisopropylidene)diphthalic anhydride,

F-PNB — difluorocyclopropane-containing polynorbornene,

F-PTMSNB — difluorocyclopropane-containing polytrimethylsilylnorbornene,

$J_i$ — $i$th component flux,

$l$ — membrane thickness,

MCr — membrane crystallization,

MD — membrane distillation,

ME — membrane emulsification,

MF — microfiltration,

$P$ — gas permeability coefficient,

PFMNB — poly[5,5-difluoro-6,6-bis(trifluoromethyl)-norbornene],

PI — polyimide,

PNB — polynorbornene,

POFPNB — poly[5,5,6-trifluoro-6-(heptafluoropropoxy)norbornene],

PTFE — polytetrafluoroethylene,

PTMSNB — poly(5-trimethylsilylnorbornene),

PV — pervaporation,

PVDF — poly(vinylidene fluoride),

PVTMS — polyvinyltrimethylsilane,

$S$ — gas solubility coefficient,

VDF — vinylidene fluoride,

UF — ultrafiltration.

## 2. Membrane gas separation principles

The membrane gas separation is performed in so-called non-porous polymer membranes, *i.e.*, membranes in which the selective diffusion layer does not contain open pores larger than several tenths of a nanometer. The separation is induced by the concentration gradient at the two membrane surfaces. The selective gas and vapour separation in non-porous materials is interpreted in terms of the solution–diffusion model proposed back in the 19th century. According to this model, the penetrant is dissolved in the membrane material near its inlet surface and then diffuses under the action of the arising concentration gradient. The permeability coefficient ($P$) serves as the measure of mass transfer through a membrane. In the SI system, the permeability coefficient is defined as the number of moles of the penetrant that passed through 1 $m^2$ area of a 1 m-thick porous sample in 1 s at a pressure drop of 1 Pa (mol $m^{-2}$ m $s^{-1}$ $Pa^{-1}$); in the literature, it is usually expressed in Barrers [1 Ba = $10^{-10}$ $cm^3$ cm $cm^{-2}$ $s^{-1}$ (cm Hg)$^{-1}$]. The thickness of the selective layer in the separation membranes is, most often, unknown; therefore, the GPU value is used for characterization [1 GPU = $10^{-6}$ $cm^3$ $cm^{-2}$ $s^{-1}$ (cm Hg)$^{-1}$]. A condition ensuring high permeability is a large gas diffusion coefficient ($D$) of the membrane material. This is a necessary but not a sufficient condition: the $P$ value also depends on the ability of the membrane material to absorb the penetrant, *i.e.*, by the penetrant solubility coefficient ($S$). Thus, we arrive at the key expression for membrane gas separation (and the solution–diffusion model)

$$P = DS \tag{1}$$

The solution–diffusion model discloses the physical meaning of the permeability coefficient $P_i$. If the mass transfer through a membrane is described by Fick's law, then the flux of the $i$th component ($J_i$) through a membrane of thickness $l$ can be expressed as

$$J_i = D_i \frac{c_{i0(m)} - c_{il(m)}}{l} \tag{2}$$

where $D_i$ is the concentration-averaged diffusion coefficient, $c_{i0(m)}$ and $c_{il(m)}$ are the penetrant concentrations in the membrane surface layer on the feed side and on the permeate side, respectively.

According to Henry's law, the concentration of the $i$th component on the membrane surface on the feed side is defined as

$$c_{i0(m)} = S_i p_{i0} \tag{3}$$

where $S_i$ is the solubility coefficient of the $i$th component, $p_{i0}$ is the pressure of the $i$th component on the feed side.

Likewise, it is possible to write down the expression for the concentration of the $i$th component $c_{il}$ on the permeate side of the membrane surface

$$c_{il} = S_i p_{il} \tag{4}$$

where $p_{il}$ is the $i$th component pressure on the permeate side. Substitution of Eqns (3) and (4) into Eqn (2) gives

$$J_i = \frac{D_i S_i (p_{i0} - p_{il})}{l} \tag{5}$$

Thus, the flux through the membrane is directly proportional to the pressure drop of the *i*th component and inversely proportional to the membrane thickness.

The gas permeability coefficients of polymer materials vary within 3–8 orders of magnitude depending on the penetrant nature. For example, oxygen permeability coefficient is in the range from $10^{-4}$ to $10^{4}$ Barrers, while helium permeability varies over a narrower range. The $P$ value is usually considered as a constant for the polymer–gas system at a constant temperature.

The solubility coefficient, which determines the concentration gradient at a given pressure drop, is a thermodynamic characteristic of permeability, whereas the diffusion coefficient is a kinetic factor, which determines the penetrant mobility in the membrane material.

It is clear that highly permeable polymers are preferred as materials for the manufacture of membranes. However, in view of the need to separate mixtures, the selectivity, or the separation factor, is equally important

$$\alpha_{ij} = \frac{P_i}{P_j} \qquad (6)$$

This parameter determines the degree of enrichment of a binary system with the *i*th component relative to the *j*th component upon a single passage of the gas through the membrane. The greater the $\alpha_{ij}$ value, the higher the concentration of the *i*th component in the permeate. With this definition of $\alpha_{ij}$, the transfer rate of a pure penetrant is assumed to be the same as the transfer rate of the same compound as a mixture component. However, this is not always the case.[14]

It is clear that high gas permeability should be inherent in polymers that have high diffusion and solubility coefficients. However, the requirements imposed on 'good' membrane materials include a combination of high permeability and selectivity values. According to an empirical rule, highly permeable materials have low selectivity. A classical and representative demonstration of this trend was reported by Robeson[15] in 1991 and repeated in 2008 [16] as a dependence of the selectivity $\alpha(A/B) > 1$ on the permeability coefficient $P(A)$ for various pairs of gases A and B in numerous polymers. For the pairs of gases considered in these studies, higher $P$ values are inherent in smaller-size molecules, *i.e.*, $P$ values vary in these systems similarly to $D$. These systems are characterized by diffusion (or kinetic) selectivity. For some polymers and gas pairs, higher permeability coefficients are observed for larger-size molecules, for example, $P(C_4H_{10})/P(CH_4) > 1$. This is defined as the thermodynamic selectivity.[17] It is important that thermodynamically selective systems show simultaneous increase in the permeability and selectivity.

## 3. Direct gas-phase fluorination of polymers

The direct gas-phase fluorination of polymers is the most natural process for the preparation of fluorinated and, perhaps, perfluorinated membrane materials. The works along this line were started in the 1980s and were actively pursued in the next decades. They were stimulated by the high reactivity of the $F_2$ molecule, which enabled treatment of polymers with different chemical structures. However, this brought about procedural complications associated with high requirements to the reactor and sealing materials and even to the fore-pump oil. All direct fluorination reactions are diffusion-controlled: the reaction proceeds on the surface of the polymer film, which is in contact with the gas phase containing $F_2$. As the fluorine gas-treated layer is thickened, the reaction slows down. The composition of the resulting polymer can also change (because of the change in the F : C and F : H atomic ratios). The growth kinetics of a new polymer layer has been extensively studied using Fourier transform IR spectroscopy, laser interferometry and other specially modified procedures.[18–20] Thus, all direct fluorination products are layered membranes with a composition gradient, *i.e.*, with different ratios of the C–H and C–F bonds across the membrane. The quantitative investigation of such objects, in particular, measurement and interpretation of their transport parameters, is a difficult task. These and other aspects are considered in detail in Thesis works.[18,21]

Direct gas-phase fluorination and subsequent studies of the gas transport and other physicochemical properties were performed for various polymers. Fluorination was investigated in detail for polyolefins (polyethylene,[18–20,22,23] polypropylene,[24–26] polymethylpentene[27]), polystyrene,[28] polyacetylenes,[29] polysulfone,[30,31] poly(phenylene oxide),[32] polyimides (for example, Matrimid[18,21]), polyvinyltrimethylsilane (PVTMS),[18,21,33,34] polydimethylsiloxane,[35] nitrile rubber[36] and other polymers and copolymers.

Despite this high diversity of the studied polymers, the elementary reactions that predominate in the fluorination are the same in all cases: the C–H bonds in the polymers are replaced by C–F bonds, the C=C double bonds are saturated with fluorine and so are the aromatic carbon–carbon bonds. Cross-linking of macrochains can also take place under the action of $F_2$.[18] If the polymer molecule contains C–N bonds (as in polyimides and polyamides) or C–Si bonds (as in some important membrane materials), they are cleaved under the action of fluorine and then the fluorine atom adds to the carbon atom. Meanwhile, the ester bonds, for instance, in poly(methyl methacrylate) are apparently retained upon fluorination.[18] When the fluorinating system contains oxygen (as either an impurity or admixture), a controlled number of C=O-containing groups is formed, in particular, a C(O)F group, which can be converted to the COOH group on contact with oxygen.

The composition of the fluorine-containing polymer layer thus formed was studied by spectroscopic methods (such as electron spectroscopy for chemical analysis, X-ray photoelectron spectroscopy and Fourier transform IR spectroscopy). In many cases, the results of these studies attest to a high degree of C–H bond replacement by C–F bonds. Certain opportunities for the control over the fluorination kinetics are provided by variation of the total pressure of the gas mixture (most often, molecular fluorine is diluted with helium or nitrogen) or the fluorine content in the mixture (usually from 0.2% to 2%).

Different polymers show different reactivities towards fluorine. Thus in the case of polymethylpentene and long reaction times, the backbone is fluorinated to a degree of 2/3 and the side groups (except for methyl) are also fluorinated to give the $CF_2CF(Me)CF_2H$ groups.[27] A high degree of fluorination is attained in several minutes. Meanwhile, in the case of polyethylene, the reaction proceeds to a higher degree only when the reaction time is about 10–12 h.[27] Probably, this is attributable to different rates of fluorine transport in these polyolefins. The reaction with

polyethylene is retarded at long reaction times. Interestingly, the helium permeability does not change with increasing degree of fluorine treatment of the film, while permeability for gases such as $CO_2$ and $CH_4$ sharply decreases. This entails a considerable increase in the selectivity, $P(He)/P(CH_4)$ and $P(He)/P(CO_2)$, respectively; the former value reaches $\sim 100$.

Contradictory results were obtained for the direct fluorination of PVTMS.[18,21,33] The fluorination of dense 23–200 μm films with 0.02%–2% fluorine–helium mixtures led to a minor decrease in the $N_2$, $O_2$, $CH_4$, $CO_2$, Kr and Xe permeability coefficients, whereas the helium permeability did not decrease. The ideal selectivity values for He, $CO_2$, Kr and Xe over $N_2$ or $CH_4$ increased, while the permeability for the $O_2-N_2$ pair remained invariable. The experiments with a composite membrane with a 0.5 μm-thick selective layer gave similar results: the membrane selectivity increased and permeability decreased with increasing treatment time. However, the selectivity for the $He-CH_4$ pair attained in these experiments (10–11) was much lower than that for fluorinated polyethylene. Different results were obtained in the fluorination of PVTMS with mixtures containing substantially more $F_2$ (33%), with oxygen (40%) being added to the gas mixture, and with subsequent grafting of acrylonitrile (AN) to the membranes: the selectivity of separation of gas pairs increased 138-fold for $He-CH_4$ and 19-fold for $CO_2-CH_4$ and $He-N_2$, with helium permeability slightly decreasing. Some of the results are presented in Table 1.

It is of interest that fluorination was carried out not only for homogeneous or composite membranes, but also for membranes assembled into a ready module. As a result, the so-called upper bound of the Robeson diagrams was overcome in some cases.[15] Similar results were obtained for the polyimide Matrimid 5218. In some experiments, even higher selectivity was attained for the $He-CH_4$ pair (6720).[18]

How does direct fluorination affect the transport properties of other polymers? A study of a polysulfone-based composite membrane showed that fluorination decreases the permeability for the transport of all gases (to a lesser extent, for helium and hydrogen). As a result, the $He-CH_4$ and $H_2-CH_4$ selectivity increases at high degrees of fluorination.[30,31] A similar effect was observed for the fluorination of poly(phenylene oxide).[32] In this case, the selectivity for the $He-CH_4$ and $H_2-CH_4$ pairs increased and the selectivity for the $O_2-N_2$ pair decreased. However, this adverse effect was mitigated by deposition of a polydimethylsiloxane layer on the ready membrane. It was recommended to repeat this procedure at intervals to improve the membrane properties.

**Table 1**. Changes in the $He-CH_4$ permeability and selectivity coefficients upon direct fluorination of PVTMS.[18]

| Treatment conditions | $P$/Barrer | | $\frac{P(He)}{P(CH_4)}$ |
|---|---|---|---|
| | $CH_4$ | He | |
| Starting PVTMS | 21.0 | 204 | 8.7 |
| 2% $F_2$ + 98% He | 4.1 | 185 | 45.1 |
| 33% $F_2$ + 67% He | 1.6 | 150 | 93.8 |
| 40% $O_2$ + 60% $F_2$ | 0.1 | 120 | 1200 |
| 2% $F_2$ + 98% He with subsequent AN grafting | 0.4 | 118 | 294 |

Thus, irrespective of the nature of the polymer subjected to direct gas-phase fluorination, a general trend holds, namely, the permeabilities for gases with relatively large-size molecules (*e.g.*, methane) decreases. The decrease in the He or $H_2$ permeability is insignificant; therefore, the $He-CH_4$ and $H_2-CH_4$ selectivities markedly increase. Kharitonov[18] interpreted this result as being due to the decrease in the polymer free volume upon fluorination and also to the oxidative cross-linking of polymer chains.

The cross-linking may lead to a decrease in the transport characteristics of partly fluorinated polymers with time. Indeed, while describing PVTMS experiments, Kharitonov[18] noted no decrease in the gas permeability after completion of the process in most cases. However, Syrtsova[21] demonstrated a sharp decrease in the permeability for the treated PVTMS and polyimide Matrimid films. However, it is important that the selectivity virtually did not decrease, but even increased in some cases.

While summarizing the results of numerous observations made in the direct fluorination of chemically different polymers, note that this is a diffusion-controlled process. The process gives a macromolecular product with a variable structure, with gradients of C–F bond concentrations and degrees of fluorination being present within the polymer film, which restricted the controllability of the structure and transport properties of the reaction product. The inevitable backbone destruction and cross-linking processes have adverse effect on the properties of the resulting membrane materials.

Also, it is noteworthy that modification predominantly involves the surface layer of the polymer film being treated.[37–40] This is also important from the applied standpoint, because the goal of gas-phase fluorination of polymers is often to endow them with barrier properties. For example, fluorination of the internal surface of polyethylene fuel tanks markedly decreases the loss of petrol or gas oil during storage. The cause of this phenomenon is clear: it is known that mixtures of perfluorinated or partly fluorinated compounds with low-molecular-weight compounds often do not obey the theory of regular solutions.[12] Automotive fuel components are rather readily soluble in polyethylene. After fluorination, the solubility sharply decreases, *i.e.*, the driving force for fuel leakage through the container walls declines. Providing polyethylene tanks with barrier properties is the subject of quite a few publications (see, for example, Refs 37–44). Thus, the products of direct gas-phase fluorination of polymers possess both membrane and barrier properties.

## 4. Plasma chemical treatment of polymers

Plasma polymerization of fluorine-containing gases and vapours and plasma-chemical surface treatment are alternatives to the direct gas-phase fluorination of polymers. Drawbacks of the direct gas-phase fluorination are associated with high chemical reactivity of molecular fluorine. As a result, for designing the production units for this process, it is necessary to choose special materials and overcome other procedural difficulties (see above). In the plasma polymerization process, these difficulties disappear, since the process involves stable fluorine-containing gases and vapours. Furthermore, by varying the nature of these compounds and plasmatron conditions, one can obtain various polymer structures and, hence, control the polymer

properties. The plasma polymerization technique has already been known for several decades.[45,46] A variety of fluorine-containing gases and vapours: $CF_4$,[47–49] $SF_6$,[50] $C_2F_6$,[51] chlorofluorocarbons, chlorofluorohydrocarbons, fluorohydrocarbons,[52] pentafluorotoluene,[53] octafluorocyclobutane[54–57] and so on[58] have been used as 'monomers'.

Fluorine-containing composite membranes were prepared by plasma-chemical treatment of various organic polymers — polydimethylsiloxane,[59] PVTMS and polytrimethylsilylpropyne (PTMSP),[50] polyolefins,[60,61] nylon-6, poly(methyl methacrylate),[62] nitrile rubber[49] and so on. Fluorine-containing polymers can also be deposited on inorganic substrates.[51] All studies performed in this field can be divided into two groups.

The first group includes studies dealing with the synthesis of fluorinated polymers on the substrate surface with a change in the gas transport properties. This process bears resemblance to the direct fluorination of polymers and gives a layered structure: a layer of a new fluorine-containing polymer appears on the substrate surface, whereas deeper layers of the initial polymer remain unaffected or little affected. The chemical composition of the polymers obtained by the plasma chemical method depends substantially on the reaction conditions in the plasmatron (pressure, discharge power, time of treatment and so on). In addition, gas separation parameters often vary with time; for example, the chain cross-linking reaction continues in the obtained layer after completion of the treatment.

The second group includes studies involving hydrophobization of porous substrates ($Al_2O_3$, track-etched membranes, zeolites, *etc.*). The goal of the studies along this line in the field of membrane processes is to obtain porous membranes with enhanced hydrophobicity for membrane distillation. These issues are beyond the scope of this review and, therefore, they will be discussed only briefly.

Consider the results of studies on the plasma modification of gas transport properties. Infrared spectroscopy is the key method used to study plasma polymers;[50,51] X-ray photoelectron spectroscopy and $^{19}F$ NMR spectroscopy have also been employed. According to spectroscopic data, the composition of fluorine-containing plasma polymers depends little on the nature of fluorine-containing gas delivered to the plasmatron. This is due to the fact that gases undergo extensive destruction in the plasmatron to give the same active species (radicals and ions). Most of the plasma polymers contain CF, $CF_2$ and $CF_3$ groups. However, as indicated by Fridman,[46] in a polymer obtained by plasma chemical treatment of a mixture of hexafluoroethane and hydrogen, the CF group predominates. A study of silicon-containing polymers showed the presence of the following groups: C=CF, CF=$CF_2$, C=$CF_2$ and $CF_2-CH_2$. The radicals and ions formed in the plasma induce cleavage of the C–Si bonds, *i.e.*, treatment is accompanied by elimination of $SiMe_3$ groups.

Most of polymers obtained by plasma polymerization of fluorine-containing gases and vapours were characterized by oxygen and nitrogen permeability. According to a study of the plasma polymerization of $C_3F_6-CH_4$ mixtures,[63] oxygen permeability coefficients increased from 10 Barrer for the use of pure $C_3F_6$ plasma to 120 Barrier for a film obtained on treatment with a binary mixture. The highest $P(O_2)/P(N_2)$ selectivity equal to 2.8 was obtained for 25 mol.% concentration of $CH_4$. A detailed investigation of a plasma polymer obtained using $SF_6$ was reported by Borisov *et al.*[50] As the treatment time increased (up to 30 min), the permeability for all gases (He, $H_2$, $O_2$, $N_2$, $CH_4$ and $CO_2$) decreased, while the selectivity for the $He-CH_4$, $H_2-CH_4$ and $CO_2-CH_4$ pairs sharply increased. The permeability for some gases of plasma polymers obtained in a microwave discharge from fluorine-containing monomers with $\approx 1$ F:C atomic ratio resulted in the most selective membranes.[64] An increased solubility of $CO_2$ in these polymers was noted; this accounted for higher $CO_2-CH_4$ selectivity. However, high selectivity cannot always be attained. For example, deposition of a plasma polymer on a zeolite substrate gave rise to a membrane the selectivity of which corresponded to Knudsen diffusion.[65]

Owing to their chemical stability, plasma polymers based on fluorine-containing monomers can be used in harsh media, for example, on contact with ozone.[52] Note that usual membranes based on perfluorinated polymers are also suitable for this purpose.[66]

Surface hydrophobization studies are much more frequent, which is mainly due to the importance of energy-efficient membrane distillation process for sea water-desalination. For conduction of these processes, the pore surface of the membranes should be as hydrophobic as possible. This is attained by deposition of thin layers of fluorine-containing plasma polymers (see, for example, Refs 67–70). In this case, hydrophobicity is mainly evaluated by measurement of contact angles on the surface.

## 5. Effect of fluorine-containing groups on the gas transport properties of amorphous polymers

The difference between the transport properties of fluorinated polymers and their hydrogen analogues can be explained by the following reasons.

The greater volume of fluorinated groups is due to the difference between the covalent radii of hydrogen (0.30 Å) and fluorine atoms (0.64 Å), or their van der Waals radii (1.10 and 1.35 Å, respectively) and to the longer C–F bond (1.328–1.379 Å) compared with the C–H bond (1.070–1.096 Å); this leads to looser packing of fluorinated polymers compared with hydrogen analogues.

Fluorine-containing materials possess lower cohesive energy density, which results in weakening of interchain interactions. A low-molecular-weight compound dissolved in this material has to perform less work for chain separation. This may result, in particular, in increasing solubility of gases and vapours. It is known that perfluorocarbons used to develop artificial blood substitutes can dissolve considerable amounts of oxygen.[71]

The C–F bonds are highly polar; therefore, dipole–dipole and dipole–quadrupole interactions are possible between the diffusing agent and polymer chains, which affects the thermodynamic and transport properties of the polymer.

The strength of the C–F bonds is very high (485 kJ $mol^{-1}$) and polymer molecules containing these bonds become more thermally stable and resistant to harsh media.

### 5.1. Polycondensation materials

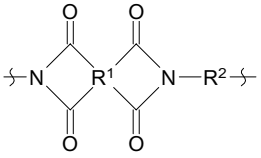
Polycondensation polymers of various classes (often combined under the common name polyheteroarylenes) have been actively studied as potential membrane materials. In

many cases, the obtained polymers contain fluorinated groups, which can be used to analyze the effect of chemical structure of these polymers on their transport properties.

### 5.1.1. Polyimides

Polyimides (PIs) are the most comprehensively investigated class of amorphous glassy polymers — potential gas separation membrane materials. The general formula of PIs can be represented by structure **1** in which $N-R^2$ implies the diamine residue and the group $R^1$ determines the dianhydride structure.

**Structure 1**



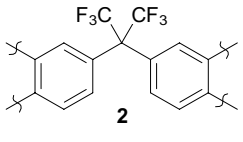
**1**

The database of the TIPC RAS contains the gas transport parameters of more than 300 homopolymes of this class, which is more than for any other class of polymers.[72] A considerable body of data is also available for copolyimides. Many of the studied PIs contain fluorinated groups. These groups can be incorporated in both dianhydrides and diamines used in the PI synthesis. A special role is played by series 6FDA dianhydrides in which the group $R^1$ has the structure represented by structure **2**.

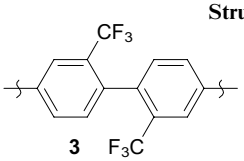
According to Tanaka and Okamoto,[73] in the permeability–selectivity diagrams, the points corresponding to PIs with this structure form the upper 'edge' of the PI cloud of points, *i.e.*, they are located most closely to the 'upper bounds' of the diagrams. The $CF_3$ groups can also be incorporated in diamines, for example, as in structure **3**.

The most permeable 6FDA-based polyimides include highly methylated diamines (durene derivatives). The dianhydride parts of PIs contain conjugated planar moieties with polar groups, resulting in strong interchain interactions, a smaller free volume and formation of charge transfer complexes, which colour polyimide films. However, when the rigid bulky $C(CF_3)_2$ groups are introduced into the dianhydride moiety, these effects are mitigated. This entails a decrease in the chain packing density, increase in the film permeability and decrease in the colour intensity.[73] In addition, the $CF_3$ groups have a relatively large volume, and in the presence of these groups, the chain packing density decreases. The introduction of $CF_3$ groups into the PI diamine moieties leads to the same effects.

**Structures 2, 3**



**2**



**3**

The data presented in Table 2 illustrate the effects of replacement of the $CMe_2$ group by $C(CF_3)_2$ in 6FDA polyimides and introduction of additional $CF_3$ groups into aromatic rings on the gas permeability and selectivity. It can be seen that the appearance of $CF_3$ groups or an increase in their number leads to a marked increase in the polymer permeability and some decrease in the selectivity.

A more pronounced permeability increase and a selectivity decrease are induced upon the introduction of bulky fluorine-containing groups $C(O)O(CH_2)_2C_6F_{13}$ into 6FDA or other polyimides (Table 3).

It may be noted that permeability increases especially sharply for the less permeable PIs taken for comparison. For 6FDA polyimides, the selectivity changes insignificantly. It is important that the $C_6F_{13}$ group has a pronounced self-plasticization effect: the glass transition temperature of polyimide **I** (see Table 3) is 290 °C (the free volume is 0.160) *versus* 205 °C (the free volume is 0.183).

**Table 2**. Effect of introduction of $CF_3$ groups into the diamine moieties of 6FDA polyimides on their gas transport and separation properties.

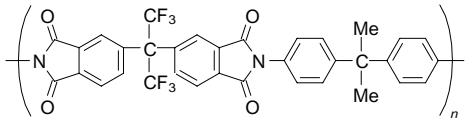
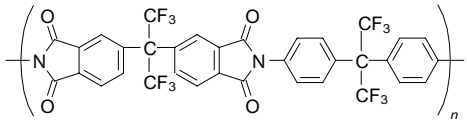
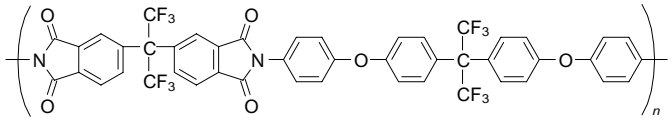
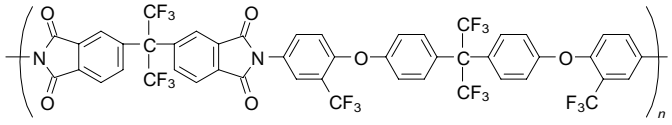
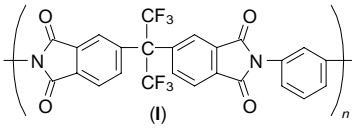
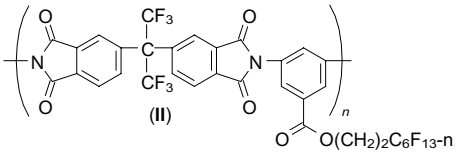
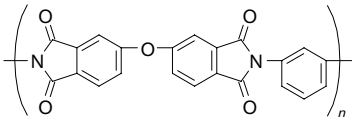
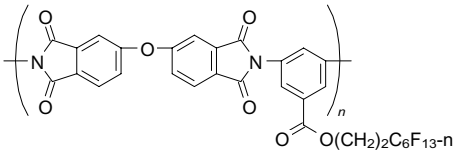
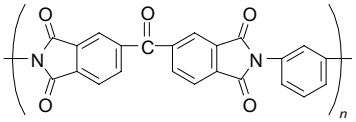
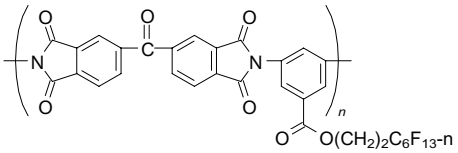
| Polymer | *P*/Barrer | | | Selectivity | | | Ref. |
|---|---|---|---|---|---|---|---|
| | $O_2$ | $N_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $CO_2-N_2$ | |
|  | 7.5 | 1.5 | 30 | 5.10 | 42.9 | 20 | 74 |
|  | 16.3 | 3.5 | 63.9 | 4.70 | 39.9 | 18.2 | 74 |
|  | 5.13 | 1.0 | 19.1 | 5.23 | 36.7 | 19.1 | 75 |
|  | 6.5 | 1.3 | 22.8 | 5.00 | 32.4 | 17.5 | 75 |

**Table 3**. Effect of introduction of bulky fluorine groups into polyimides on their gas transport and separation properties.[76]

| Polymer | *P*/Barrer | | | Selectivity | | |
|---|---|---|---|---|---|---|
| | $O_2$ | $N_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $CO_2-N_2$ |
|  (I) | 2.55 | 0.38 | 9.7 | 6.7 | 46.3 | 25.6 |
|  (II) | 4.74 | 0.74 | 17.8 | 6.4 | 40.4 | 24.0 |
|  | 0.081 | 0.012 | 0.30 | 6.8 | 47.3 | 25.1 |
|  | 2.61 | 0.56 | 11.0 | 4.9 | 30.6 | 19.7 |
|  | 0.11 | 0.016 | 0.43 | 7.0 | 49.8 | 26.8 |
|  | 2.20 | 0.48 | 10.1 | 4.6 | 34.8 | 21.0 |

The greater free volume accounts for the higher gas permeability of polymer **II**.

Similar effects of introduction and increase in the concentration of $CF_3$ groups were also noted for PIs based on other dianhydrides (Tables 4 and 5).

**Table 4**. Effect of introduction of $C(CF_3)_2$ and $CF_3$ groups into the diamine moieties of BPDA polyimides on their gas transport and separation properties.

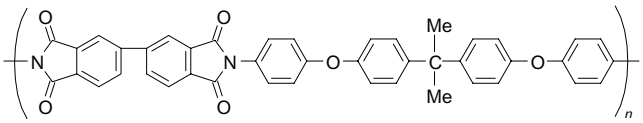
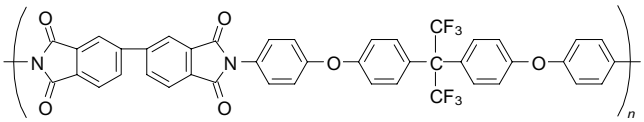
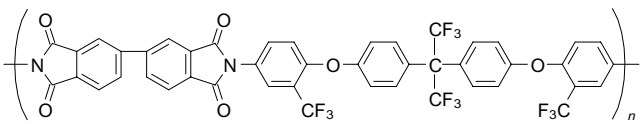
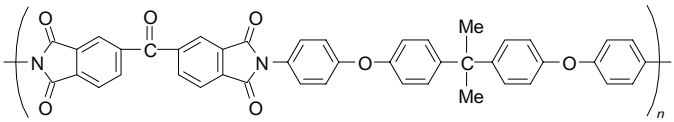
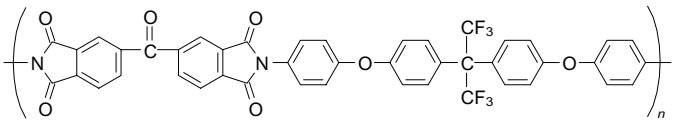
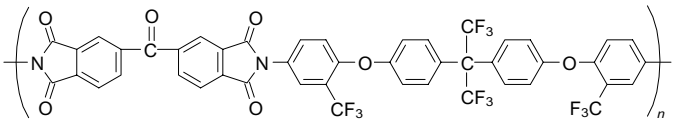
| Polymer | *P*/Barrer | | | Selectivity | | | Ref. |
|---|---|---|---|---|---|---|---|
| | He | $O_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $He-CH_4$ | |
|  | 7.5 | 0.596 | 0.0846 | 6.35 | 33.1 | 88.7 | 77 |
|  | 18.3 | 1.67 | 7.33 | 5.48 | 33.9 | 84.7 | 77 |
| | – | 1.54 | 4.96 | 6.29 | 34.2 | – | 74 |
|  | – | 3.11 | 9.15 | 5.52 | 23.9 | 32.8 | 74 |

**Table 5**. Effect of introduction of $C(CF_3)_2$ and $CF_3$ groups into the diamine moieties of BPDA polyimides on their gas transport and separation properties.

| Polymer | *P*/Barrer | | | Selectivity | | | Ref. |
|---|---|---|---|---|---|---|---|
| | $O_2$ | $N_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $CO_2-N_2$ | |
|  | 0.508 | 0.070 | 2.47 | 7.21 | – | 35.3 | 78 |
|  | 1.14 | 0.26 | 4.37 | 5.85 | 42.2 | 16.8 | 74 |
|  | 2.17 | 0.31 | 6.94 | 5.86 | 34.2 | 22.4 | 74 |

Lots of publications are devoted to 6FDA and other polyimides with fluorine-containing groups; some information can be found in Refs 77–84. In some cases, the effects of introduction of fluorine-containing groups are camouflaged by effects of other design elements. This is shown, for example, in a series of works,[85–90] in which the authors synthesized and investigated polyimides with bulky substituents.

Polyimides considered above are linear polymers. Gao *et al.*[91] prepared a hyperbranched PI based on 1,4-bis(3,4-dicarboxyphenoxy)benzene as the dianhydride monomer and 1,3,5-tris(4-amino-2-trifluoromethylphenoxy)benzene as the triamine monomer using 3,5-bis(trifluoromethyl)aniline as the terminal groups. In this case, too, an increase in the concentration of $CF_3$ groups increased gas permeability; however, this effect was less pronounced than in the case of linear PIs: the $P(CO_2)$ value increased from 1.5 to 2.7 Barrer.

### 5.1.2. Polyamides

Similar data on the influence of the $CF_3$ groups on the gas permeability were obtained for aromatic polyamides. Some data are presented in Table 6. The polymers included in the Table contain bulky substituents, which increase the free volume and, hence, gas permeability. Nevertheless, even against the background of these pronounced effects, the presence of the $C(CF_3)_2$ group in polyamide leads to a substantial increase in the permeability coefficients with some (often minor) decrease in the selectivity.

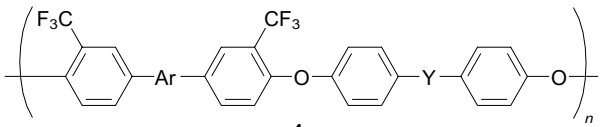
Other polyamides of various structures with fluorine-containing groups have been synthesized and studied.[94–100]

### 5.1.3. Other polycondensation materials

The above-noted influence of the $C(CF_3)_2$ groups on the gas permeability is observed not only for PIs, but also for polyether ether ketones (Table 7) and polyesters (Table 8).

However, unlike PIs, in the case of polyether ether ketones and polyesters, the introduction of the $C(CF_3)_2$ groups increases the permeability and slightly increases the selectivity for $CO_2$-containing pairs of gases. Polyarylene ethers (structure **4**) are also prepared by polycondensation, particularly, involving bis-phenols and dihalogen-containing compounds. The diverse structures of polymers formed upon the variation of groups Ar and Y and the properties of these materials are covered in a review.[7] The most detailed studies are available for polymers that were prepared in order to develop materials with desired optical and electrical properties (optical wave guide materials, polymers with low dielectric constant, *etc.*). However, in some cases, membrane properties of polymers of this class were also studied.

**Structure 4**



**4**

As applied to fluorine-containing polymers, studies mainly concerned the effects of replacement of $CMe_2$ groups in the backbone by $C(CF_3)_2$ groups. This replacement leads to increasing chain rigidity (increasing glass transition temperature) and permeability, which is often not accompanied by decreasing selectivity of gas separation.[103–108]

The data presented in Table 9 indicate that, like in other cases, $C(CF_3)_2$ groups present in the backbone increase (although slightly) the gas permeability. This increase in the permeability is mainly caused by increasing the diffusion coefficients.[109] Similar insignificant effects were observed for polyarylene ethers with fluorine atoms in the aromatic structures. The condensation of decafluorobiphenyl with 1,3-dihydroxybenzene and 4-[4-(4-hydroxyphenoxy)-2,3,5,6-tetrafluorophenoxy]phenol afforded two polymers, one of which occupied a more favourable position in the Robeson diagram for $He-H_2$ and $He-CH_4$ pairs of gases.[110]

Polyarylene ethers with fluorine-containing moieties, in particular, those containing $CF_3$ groups and bulky substituents have been studied.[108–110]

**Table 6**. Gas permeability coefficients and gas separation selectivities for polyamides containing a $C(CF_3)_2$ group.

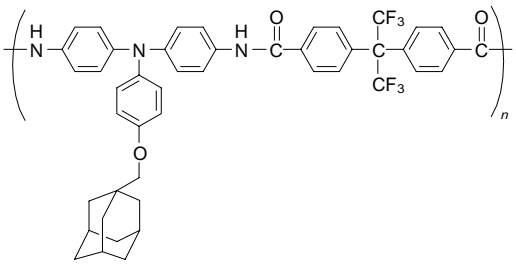
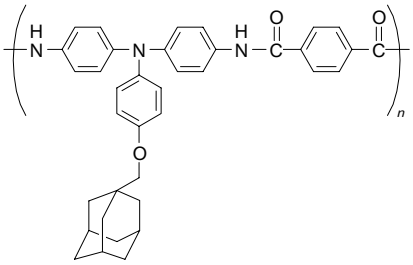
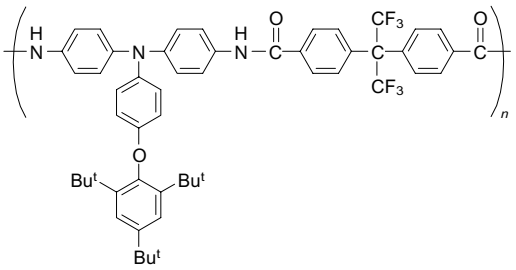
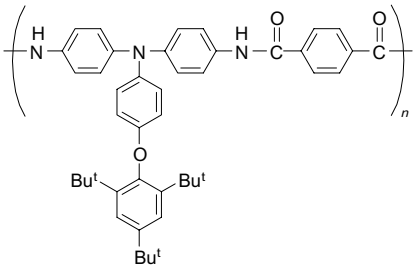
| Polymer | *P* /Barrer | | Selectivity | | Ref. |
|---|---|---|---|---|---|
| | $CO_2$ | $O_2$ | $CO_2-CH_4$ | $O_2-N_2$ | |
|  | 61.5 | 14.2 | 51.25 | 10.14 | 92 |
|  | 14.5 | 3.8 | 48.33 | 9.50 | 92 |
|  | 119.0 | 29.0 | 37.19 | 9.67 | 93 |
|  | 51.0 | 12.8 | 24.28 | 7.53 | 93 |

**Table 7**. Effect of the replacement of $CMe_2$ groups by $C(CF_3)_2$ groups in polyether ether ketones on their gas transport and separation properties.[101]

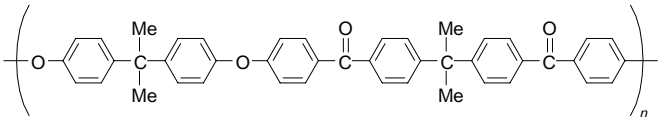
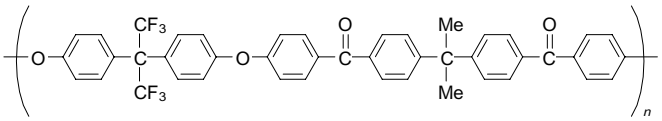
| Polymer | *P* /Barrer | | | Selectivity | | |
|---|---|---|---|---|---|---|
| | He | $O_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $He-CH_4$ |
|  | 12.4 | 1.1 | 4.6 | 5.24 | 20 | 53.9 |
|  | 26.4 | 2.4 | 8.6 | 5.45 | 23.2 | 71.4 |

**Table 8**. Effect of the replacement of $CMe_2$ groups by $C(CF_3)_2$ groups in polyesters on their gas transport and separation properties.[102]

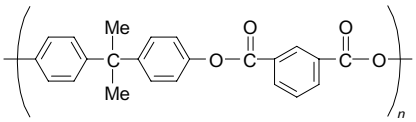
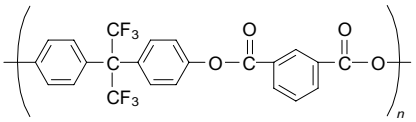
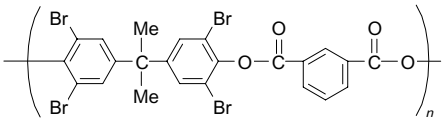
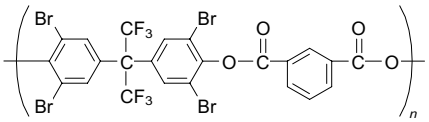
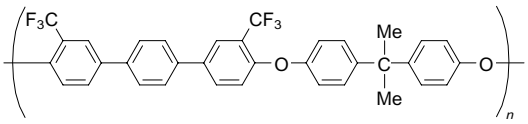
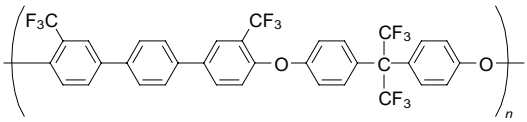
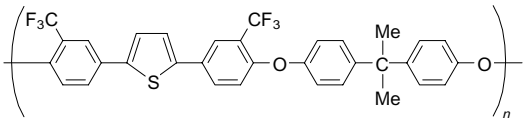
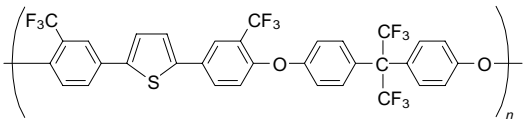
| Polymer | *P*/Barrer | | | Selectivity | | |
|---|---|---|---|---|---|---|
| | He | $O_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $He-CH_4$ |
|  | 13.4 | 1.33 | 5.4 | 5.54 | 23.2 | 57.5 |
|  | 47.8 | 5.23 | 19.1 | 4.71 | 23.9 | 59.8 |
|  | 18.3 | 1.3 | 4.93 | 7.22 | 34.7 | 115 |
|  | 66.3 | 6.75 | 25.6 | 6.31 | 42.9 | 111 |

**Table 9**. Effect of $C(CF_3)_2$ groups in polyarylene ethers on their gas transport and separation properties.[103, 105]

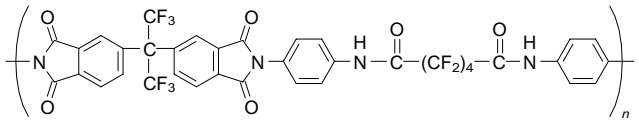
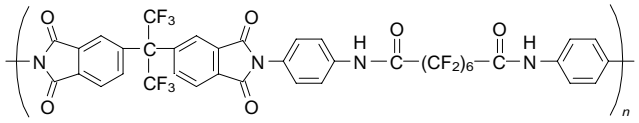
| Polymer | *P*/Barrer | | Selectivity | |
|---|---|---|---|---|
| | $O_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ |
|  | 7.1 | 30.3 | 3.88 | 16.1 |
|  | 9.6 | 37.3 | 3.48 | 16.7 |
|  | 4.8 | 18.5 | 3.47 | 13.1 |
|  | 7.0 | 25.3 | 3.19 | 16.0 |

The effect of fluorine-containing groups introduced into polymer side chains or backbone was studied for polycondensation materials. For example, the introduction of $CF_2$ groups into the backbone was studied for polyamidoimides.[111] The increase in the number of these groups from four to six induced some increase in the permeability and a slight increase in the selectivity for $CO_2$-containing pairs of gases (Table 10).

In some cases, certain design elements of fluorine-containing polymers considerably affect the transport properties. Examples are polycondensation materials (in particular, polyimides and polyethers) of intrinsic microporosity.[112–115] In particular, polymers containing a $C(CF_3)_2$ group connected to a rigid ladder structure has higher gas permeability than 6FDA-based polymers, so that the data points mapped in the Robeson diagrams[16] are above the upper bound of 2008.[114, 115]

Thus, numerous data for polycondensation materials attest to the influence of fluorine-containing groups on the gas transport and separation properties of polymers. How-

**Table 10**. Effect of introduction of $CF_2$ groups into the polyamidoimide backbone on the gas transport and separation properties.[111]

| Polymer | *P*/Barrer | | | Selectivity | | |
|---|---|---|---|---|---|---|
| | $O_2$ | $N_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-CH_4$ | $CO_2-N_2$ |
|  | 1.49 | 0.27 | 5.72 | 5.52 | 47.7 | 21.2 |
|  | 1.9 | 0.39 | 8.91 | 4.87 | 52.4 | 22.8 |

ever, it is worth noting that the observed effects are often moderate, and the increase in the gas permeability is, in most cases, accompanied by a decline of the separation selectivity.

## 5.2. Polyacetylenes

Among the membrane materials applicable for the separation of gases and vapours, polyacetylenes occupy a special place. The most gas permeable polymers belong exactly to this class of amorphous glassy polymers.[116] For polyacetylenes, the relationship between the monomer unit structure and transport properties of materials was followed in detail. High gas permeability appears in the presence of bulky nonpolar substituents (preferably, $SiMe_3$ groups) attached directly to the polymer backbone.[116–118] The gas permeability of polyacetylenes varies over rather broad limits: for example, oxygen permeability coefficients range from 18 000 to 3.8 Barrer.[117] The gas permeability of polyacetylenes can also be controlled by other structural design elements. In particular, this refers to fluorine-containing substituents, represented, most often, by fluorine atoms or $CF_3$ groups.[118–123] Cases of inclusion of more bulky fluorinated groups into the monomer units of polyacetylenes are also known.[124]

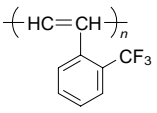
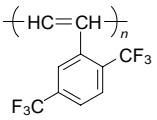
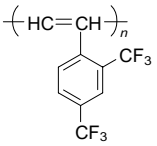
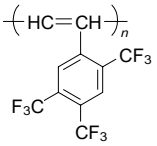
The introduction of several fluorinated groups into polyacetylenes increases the gas permeability, which is more pronounced than that for other classes of polymers. This is illustrated by data presented in Table 11. It can be seen that polyacetylenes containing di- or trisubstituted benzene side groups possess gas permeability coefficients an order of magnitude higher than those for the polymer with one $CF_3$ group. The permeability also depends on the spatial substitution pattern of disubstituted polyphenylacetylenes.

Masuda *et al.*[123] studied in detail the permeability of polyphenylacetylene containing only one $CF_3$ group for a number of gases. The permeability coefficients (Barrer) were measured for the following gases:

| *P*(He) | *P*($H_2$) | *P*($O_2$) | *P*($N_2$) | *P*($CO_2$) | *P*($CH_4$) |
|---|---|---|---|---|---|
| 130 | 140 | 25 | 7.3 | 130 | 6.6 |

The effect of introduction of fluorine-containing groups is less pronounced if the polyacetylene molecule contains other substituents (first of all, $SiMe_3$) that sharply affect the gas permeability. This is indicated, in particular, by the data of Sakaguchi *et al.*,[119] who studied polydiphenylacetylenes containing one or two fluorine atoms as substituents in the benzene ring (Table 12).

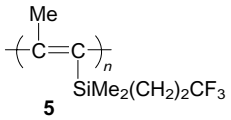
**Table 11**. Effect of introduction of $CF_3$ groups into elementary units of polyacetylenes on their gas transport properties.[121]

| Polymer | *P*/Barrer | | $\frac{P(O_2)}{P(N_2)}$ |
|---|---|---|---|
| | $O_2$ | $N_2$ | |
|  | 32 | 7.6 | 4.2 |
|  | 450 | 196 | 2.3 |
|  | 160 | 59 | 2.7 |
|  | 780 | 370 | 2.1 |

Ideal selectivity values presented in Tables 11 and 12 demonstrate the clear compensation effect for polyacetylenes with fluorine-containing groups — more permeable materials are less selective.

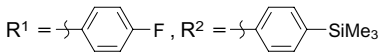
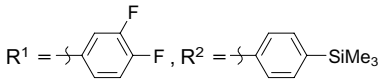
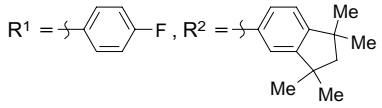
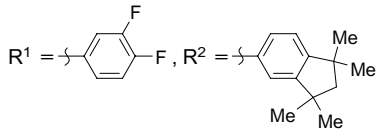
Fluorine groups can be introduced not only as substituents in the aromatic rings; they can also be attached to the carbon atom of the aliphatic moiety. An example is provided by poly(trifluoropropyldimethylsilyl)prop-1-yne (structure **5**), which has rather high ideal selectivity. Thus $\alpha(CO_2/CH_4) = 12.7$, which is higher than this value for polytrimethylsilylpropyne (2.07).[126]

**Structure 5**



**5**

**Table 12**. Gas permeability of polydiphenylacetylenes with the general formula $-(-R^1C{=}CR^2-)_n-$.

| *P* /Barrer | | $\frac{P(O_2)}{P(N_2)}$ | Ref. |
|---|---|---|---|
| $O_2$ | $N_2$ | | |
|  | | | |
| 2900 | 1900 | 1.5 | 119 |
|  | | | |
| 3600 | 2400 | 1.5 | 119 |
|  | | | |
| 17 900 | 15 600 | 1.2 | 125 |
|  | | | |
| 18 700 | 16 600 | 1.1 | 125 |

## 5.3. Metathesis polymers

Metathesis polynorbornenes are among the best studied classes of amorphous glassy carbochain polymers. The interest in these compounds is related to the development of materials for gas separation membranes.[10, 127, 128] Depending on the chemical structure of the backbone, three subclasses can be distinguished: proper polynorbornenes (PNB), polytricyclononenes and dicarboximide polynorbornenes. They all have a ring-chain structure of the backbone. The physicochemical and transport properties of these polymers can be varied by substitution of the five-membered ring, in particular, by introduction of the bulky $SiMe_3$ group. Numerous polymers with C–F bonds being introduced in place of the C–H bonds or with other fluorine-containing substituents have been studied. Below we consider the effects of such modifications of polynorbornenes.

It was shown [129, 130] that the introduction of a $CF_3$ or $OC_3F_7$ group into the five-membered ring of polynorbornene substantially increases the gas permeability of the polymer (Table 13). Relatively high gas permeability coefficients, considerably exceeding those of unsubstituted polynorbornene, were found for poly[5,5-difluoro-6,6-bis(trifluoromethyl)norbornene] (PFMNB) and poly[5,5,6-trifluoro-6-(heptafluoropropoxy)norbornene] (POFPNB).

Using the positron annihilation method, increased free volume was found in both polymers. The structure of substituents affected the flexibility of chains: a higher glass transition temperature was inherent in PFMNB (169 °C) than in POFPNB (77 °C), which is apparently caused by self-plasticization by $OC_3F_7$ groups.

For the methane–ethane penetrant pair, the inequality $P(CH_4) > P(C_2H_6)$ holds, *i.e.*, the selectivity is diffusion-controlled. A study of sorption isotherms showed that in the case of PNB, the isotherm for $C_2H_6$ is located above the isotherm for $CO_2$ (the usual order for glassy polymers). However, for both fluorinated polymers, the opposite arrangement of sorption isotherms for these gases is observed. This result is one of the first indications of the reduced affinity of hydrocarbons to fluorinated or perfluorinated polymers.[12]

The same conclusion follows from analysis of the selectivity data for fluorinated polymers (see Table 13).

The synthesis and transport properties of dicarboximide metathesis polymers have been reported.[131–135] The permeability coefficients of some of the prepared polymers with fluorine-containing substituents are presented in Table 14. These polymers are not distinguished by high gas permeability. The highest $P(O_2)$ value was found for the polymer with two $CF_3$ substituents. The presence of only one $CF_3$ group in the benzene ring has a minor effect on the permeability. A comparison of the $P(CH_4)$ and $P(C_2H_6)$ values demonstrated that, like in other cases, the separation of hydrocarbons is diffusion-controlled.

The effects of fluorination of four-membered rings in polytricyclononenes have been investigated.[137, 138] Some results are presented in Table 15.

Fluorine modification is possible not only for the five-membered ring of metathesis polynorbornenes, but also for

**Table 13**. Permeability coefficients and separation selectivities for gas pairs and fluorinated metathesis polynorbornenes.[130]

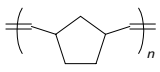
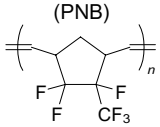
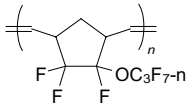
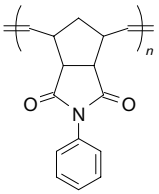
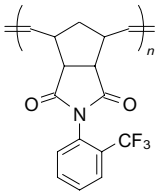
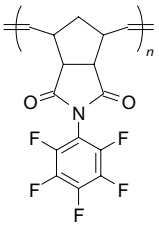
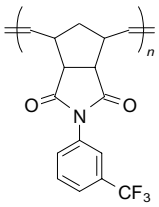
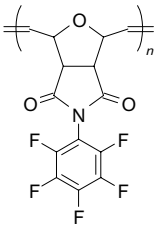
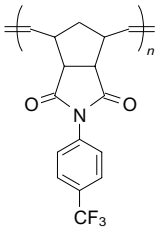
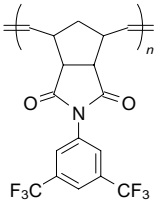
| Polymer | *P* /Barrer | | | | | | Selectivity | | |
|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ | $O_2-N_2$ | $H_2-CH_4$ | $CO_2-CH_4$ |
|  (PNB) | 21 | 2.8 | 1.5 | 15.4 | 2.5 | 1.4 | 1.9 | 8.6 | 6.3 |
|  (PFMNB) | 166 | 50 | 17 | 200 | 13 | 6.6 | 2.9 | 12.7 | 15.4 |
|  (POFPNB) | 130 | 55 | 17 | 200 | 18 | 14 | 3.2 | 6.5 | 11 |

**Table 14**. Permeability coefficients for various gases in dicarboximide metathesis polynorbornenes and polyoxonorbornene with fluorine substituents.[135, 136]

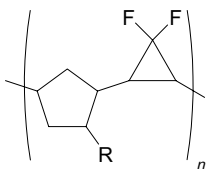
| Polymer | *P* /Barrer | | | | | | Polymer | *P* /Barrer | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ | | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $C_2H_6$ |
|  | 11.0 | 1.44 | 0.31 | 11.44 | 0.54 | 0.09 |  | 39.25 | 5.63 | 1.30 | 34.61 | 1.48 | – |
|  | 38.5 | 6.08 | 1.55 | 25.17 | 1.37 | 0.70 |  | 15.1 | 1.8 | 0.36 | 9.83 | 0.37 | – |
|  | 19.55 | 2.66 | 0.59 | 16.51 | 0.64 | 0.35 |  | 34.42 | 6.17 | 1.47 | 34.37 | 1.59 | – |
|  | 57.41 | 13.53 | 4.20 | 67.26 | 4.28 | 2.62 | | | | | | | |

the double bond. This reaction was accomplished for unsubstituted polynorbornene and for polytrimethylsilylnorbornene (PTMSNB).[139] This yielded difluorocyclopropanated polymers (structure **6**) — F-PNB and F-PTMSNB, respectively.

The data in Table 16 indicate that in this case, too, the permeability markedly increases; this especially refers to unsubstituted PNB. It is of interest that the increase in the permeability is not accompanied by a noticeable decrease in the selectivity.

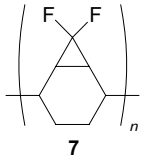
A polymer containing a three-membered ring with the $CF_2$ group has been synthesized and described[140] (structure **7**).

**Structures 6, 7**



**6**

R = H or $SiMe_3$



**7**

Thus, unlike direct and plasma fluorination, the modification of norbornene polymers with fluorine-containing groups is not accompanied by a decrease in the gas permeability. This may be attributable to the fact that this modification method does not generate cross-links in the resulting polymer matrix.

### 5.4. Fluorinated polystyrenes

The data on fluorinated polystyrene derivatives are much less abundant than the data on similar derivatives of the polymers considered above. Nevertheless, they can also be used to follow the effect of concentration of the C – F bonds on the transport properties. The permeability coefficients are given in Table 17.

It can be seen that with increasing concentration of the C – F bonds in the monomer unit of the polymer, the permeability increases. The most permeable polymer among the studied ones contains a silicon atom in the substituent. As can be seen by examining Table 17, more permeable polymers are less selective.

### 5.5. Fluorinated ethyl cellulose derivatives

Data on the gas permeability of fluorine-containing cellulose derivatives have been published. In a study of Khan *et al.*,[144] ethyl cellulose derivatives (structure **8**) with

**Table 15**. Permeability coefficients for various gases and gas separation selectivities for metathesis polytricyclononenes with fluorinated substituents.[137]

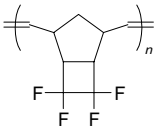
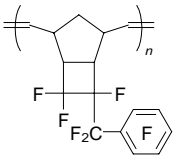
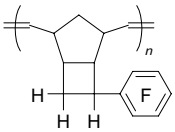
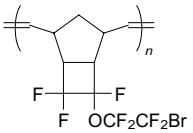
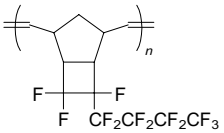
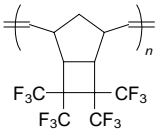
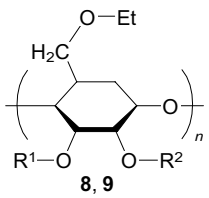
| Polymer | $T_c$/°C | *P*/Barrer | | | | | | Selectivity | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | He | $H_2$ | $N_2$ | $O_2$ | $CO_2$ | $CH_4$ | $O_2-N_2$ | $CO_2-N_2$ | $CO_2-CH_4$ | $H_2-CH_4$ | $He-CH_4$ |
|  | 107 | 29 | 20 | 1.1 | 4.1 | 16 | 0.9 | 3.7 | 14.5 | 17.6 | 21.2 | 31.9 |
|  | 107 | 55 | 34 | 2.3 | 7.0 | 26 | 1.9 | 3.0 | 11.3 | 13.7 | 17.7 | 28.9 |
|  | 107 | 44 | 41 | 2.3 | 8.2 | 33 | 3.5 | 3.6 | 14.3 | 9.4 | 11.7 | 12.6 |
|  | 106 | 76 | 66 | 5.1 | 17 | 96 | 5.3 | 3.3 | 18.8 | 18.1 | 12.5 | 14.3 |
|  | 89 | 280 | 175 | 24 | 57 | 210 | 16 | 2.4 | 8.8 | 13.1 | 10.9 | 17.5 |
|  | 199 | 510 | 700 | 60 | 180 | 730 | 46 | 3.0 | 12.2 | 15.9 | 15.2 | 11.1 |

**Table 16**. Permeability coefficients for various gases and gas separation selectivities for non-modified and double-bond modified polynorbornenes.[139]

| Polymer | *P*/Barrer | | | | | | Selectivity | | |
|---|---|---|---|---|---|---|---|---|---|
| | He | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $He_2-CH_4$ | $O_2-N_2$ | $CO_2-CH_4$ |
| PNB | 14.9 | 18.0 | 2.3 | 0.43 | 9.3 | 0.78 | 19.0 | 5.3 | 11.9 |
| F-PNB | 35.4 | 33.3 | 5.1 | 1.1 | 23.1 | 1.5 | 23.6 | 4.6 | 15.4 |
| PTMSNB | 101 | 144 | 34 | 8.3 | 140 | 19 | 5.3 | 4.1 | 7.4 |
| F-PTMSNB | 154 | 195 | 44 | 11 | 217 | 21 | 7.3 | 4.0 | 10.3 |

~0.31 OH groups per monomer unit were allowed to react with perfluoroacyl anhydrides to give compound with the general structure **9**.

**Structures 8, 9**



**8**, **9**

**8**: $R^1$, $R^2$ = Et, H;
**9**: $R^1$, $R^2$ = Et, $CF_3C(O)$, $C_2F_5C(O)$, $C_3F_7C(O)$, $C_7F_{15}C(O)$

It was found that substitution of hydroxyl groups was quantitative. After the introduction of fluorinated substituents, the glass transition temperature increases and the free volume somewhat increases. In addition, the polymers show a substantial increase in the permeability coefficients (Table 18), which becomes more pronounced with increasing concentration of the C–F bonds in the polymer; however, the change in the selectivity was insignificant.

It was shown [144] that the increase in the permeability is due, most of all, to the increase in the diffusion coefficients.

**Table 17**. Permeability coefficients for various gases and gas separation selectivities for polystyrenes substituted with fluorinated groups.[141 – 143]

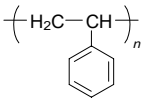
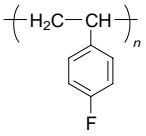
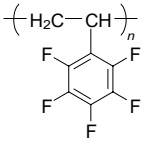
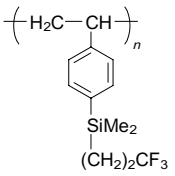
| Polymer | *P*/Barrer | | | | | | Selectivity | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | He | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $He-N_2$ | $He_2-CH_4$ | $O_2-N_2$ | $CO_2-CH_4$ |
|  | 22.4 | – | 2.9 | 0.53 | 12.4 | 0.7 | 42 | 28.3 | 5.5 | 15.7 |
|  | 34.4 | – | 4.4 | 0.8 | 117.2 | 1.06 | 42.5 | 32.5 | 5.4 | 16.2 |
|  | 88 | 65 | 14 | 5.9 | 50 | 5.1 | 14.9 | 17.2 | 2.4 | 9.8 |
|  | 95 | 109 | 38.1 | 11.8 | 284 | 22 | 8.0 | 4.3 | 3.2 | 12.9 |

**Table 18**. Permeability coefficients (Barrer) for various gases for fluorine-containing ethyl cellulose derivatives (structures **8** and **9**).[144]

| R | He | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ |
|---|---|---|---|---|---|---|
| H | 53 | 76 | 18 | 5.0 | 110 | 12 |
| $CF_3C(O)$ | 72 | 192 | 28 | 8.0 | 172 | 17 |
| $C_2F_5C(O)$ | 100 | 140 | 44 | 16 | 250 | 30 |
| $C_3F_7C(O)$ | 114 | 155 | 52 | 20 | 284 | 37 |
| $C_7F_{15}C(O)$ | 110 | 130 | 48 | 16 | 251 | 29 |

## 6. Industrial fluorine-containing polymers

The polymers considered above are synthesized and studied mainly in research laboratories and have no extensive practical application. Meanwhile, many fluorinated polymers characterized by chemical inertness, thermal stability, reduced surface energy and good dielectric properties are widely used and manufactured on an industrial scale. Polymers that have non-membrane applications were investigated for their transport properties.

Although this review is devoted to membrane properties of amorphous polymers and non-porous gas separation membranes based on them, it is necessary to say a few words about widely used partially crystallized polymers, their copolymers and the porous membranes they form. Among these materials, most attention is given to polytetrafluoroethylene $-(CF_2CF_2)_n-$ (PTFE), poly(vinylidene fluoride) $-(CF_2CH_2)_n-$ (PVDF) and diverse copolymers based on them. In some cases, the degree of crystallinity of these polymers is very high, *e.g.*, the content of the crystalline phase in PTFE is 92% – 98%.[145] As a rule, the crystalline phases are impermeable for gas and vapour molecules. As a result, the diffusion pathways, which are localized in amorphous areas of these materials, are more tortuous, resulting in lower diffusion coefficients of the penetrants. They also possess lower solubility coefficients and, hence, lower gas permeability coefficients than common amorphous polymers. However, because of the reduced interaction energy of perfluorinated chains, pore formation is possible in these materials. The presence of pass-through pores increases the gas transport velocity. Which of these two opposite trends predominates depends on the membrane moulding method and conditions.

The gas transport parameters of some partially crystalline polymers given in Table 19 confirm the above statements. All polymers and copolymers in the Table have low permeability. However, the gas separation selectivities are very different for these homopolymers. Low-permeable PTFE and Teflon FEP show also low selectivity, that is, the compensation effect between the permeability and selectivity is not observed in this case,[15, 16] probably due to the fact that these polymers are partially crystalline and have a high concentration of the crystalline phase. This dictates the gas permeability level, whereas the selectivity is affected by the properties of the amorphous phase in which the mass transfer takes place.

However, even less permeable poly(vinyl fluoride) shows a high selectivity of gas separation, in particular, for the $O_2-N_2$ pair. Poly(vinylidene fluoride) shows an unusual relationship: $P(N_2) > P(O_2)$. Poly(chlorotrifluoroethylene) was noted[147] to have an exceptionally high $He-CH_4$ selectivity ($\alpha = 1100$). In this characteristic, this partially crystalline polymer is superior to amorphous polyhexafluoropropylene ($\alpha = 549$),[148] but is more than 20 times inferior in the *P*(He) value.

Summarizing the above, it should be noted that regarding the whole set of their properties, partially crystalline fluorinated polymers should not be considered as potential gas separation membrane materials. Meanwhile, there are various ways of fabricating porous membranes from these polymers, suitable for the use in liquid separation proc-

**Table 19**. Crystallinity, permeability coefficients and selectivities for gas pairs in some partially crystalline fluorine-containing homopolymers.[9]

| Polymer | Crystallinity (%) | *P*/Barrer | | Selectivity | | | Ref. |
|---|---|---|---|---|---|---|---|
| | | $O_2$ | $N_2$ | $CO_2$ | $O_2-N_2$ | $CO_2-N_2$ | |
| PTFE (Dyneon™ TF 1750) | >90 | 3.9 | 1.3 | 11 | 2.9 | 8.1 | 9 |
| PTFE with a density of 2.18 g $cm^{-3}$ | – | 7 | 1.4 | 11.5 | – | 8.2 | 146 |
| TFE – hexafluoropropylene copolymer (Teflon FEP, Daikin Neoflon™ FEP) | 70 | 4.9 | 1.6 | 13 | 3.1 | 8.1 | See [a] |
| Poly(vinyl fluoride) (Chemmours™ Tedlar) | 35–47 | 0.02 | 0.0015 | 0.07 | 13 | 44 | See [b] |
| Poly(vinylidene fluoride) (Arkema Kynar®) | – | 0.03 | 0.04 | 0.15 | 0.7 | 3.3 | See [c] |
| Poly(chlorotrifluoroethylene) (Honeywell Aclar®) | – | 0.09 | 0.015 | 0.24 | 5.9 | 16 | 9 |
| Poly(chlorotrifluoroethylene) HydroBlock*R600TR | ~50 | – | 0.033 | 0.48 | – | 14.5 | 147 |

[a] See https://daikin-america.com/docs/FEP%20Pellets%20Brochure.pdf_g2_Brochure.pdf; [b] see http://www.dupont.com/content/dam/dupont/products-and-services/membranes-and-films/pvf-films/documents/DEC_Tedlar_GeneralProperties.pdf; [c] see http://www.plasticfilmbags.com/letters/Gas%20permeability%20of%20flouropolymers.pdf

esses.[145] These porous polymers are highly hydrophobic and, hence, they are suitable as membrane materials for processes such as membrane distillation (MD), membrane crystallization (MCr) and membrane emulsification (ME) for the preparation of oil-in-water emulsions. There are numerous methods for functionalization (hydrophilization) of these polymers. The hydrophilic membrane materials thus formed can be used for the baromembrane separation of water-based systems: microfiltration (MF), ultrafiltration (UF) and hydrophilic pervaporation.[145] This flexibility opens up prospects for solving a number of problems by membrane methods. The driving force of the MD and MCr processes is the temperature gradient,[149–152] while in the MF and UF processes, it is the pressure gradient.[153] Some summary of the processes that make use of porous, crystalline fluorine-containing membranes is given in Table 20.

There are also industrial processes for manufacturing several perfluorinated materials, tetrafluoroethylene copolymers with perfluorinated ethers, such as amorphous Teflons AF,[154] Hyflon AD copolymers,[155] proton-conducting Nafion type polymers,[156, 157] widely used in electromembrane processes and fuel cells, and other. One such copolymer, amorphous Teflon AF2400,[9, 12, 154, 158, 159] belongs to the class of highly permeable polymer materials [$P(O_2)$ = 960–1600 Barrer]. The unusual thermodynamic sorption properties of these polymers are reflected in the reduced affinity for organic compounds, in particular, hydrocarbons. Like other amorphous perfluorinated polymers,[148, 160] they are less prone to plasticization, which is responsible for low selectivity of separation of gas mixtures containing organic vapors,[12] but have enhanced selectivity for gas pairs such as $He-CH_4$.[12, 148, 158–160] These polymers showed high potential in oxygenation and ozonation of aqueous solutions,[161–163] pervaporation and reverse osmosis for separating organic mixtures that do not dissolve the membrane materials.[164, 165] More detailed consideration of these and other membrane properties of amorphous perfluorinated polymers is beyond the scope of this review.

**Table 20**. Some applications of membranes based on PVDF and PTFE.[9]

| Polymer | Processes |
|---|---|
| PVDF (homopolymer) | MF, UF, MD, MCr |
| VDF copolymers | MF, UF, MD |
| PTFE (homopolymer) | MD, PV |
| TFE copolymers [a] | MD |

[a] Also used in fuel cells and Li batteries.

## 7. Conclusion

This review demonstrates the presence of diverse methods for fluorine atom introduction into polymers. However, the application of different methods leads to different results. Direct fluorination of polymers and plasma chemical synthesis are accompanied most often by decreasing permeability and increasing gas separation selectivity. The polymers obtained from monomers containing fluorine atoms or $CF_2$ and $CF_3$ groups usually show the opposite trend: increasing gas permeability with some decrease (or retention) of the selectivity.

The key drawback of direct gas-phase fluorination of polymers under the action of molecular fluorine is the high aggressive behaviour of this reagent, which leads to partial cleavage of backbones, formation of undesirable low-molecular-weight products, cross-linking and elimination of substituents such as $SiMe_3$, which determine the valuable membrane properties of the initial polymers. These effects can be mitigated by conducting the reaction under milder conditions, for example, in solutions of perfluorinated solvents inert towards molecular fluorine. The use of milder fluorinating agents, for example, $CoF_3$ or other transition metal fluorides has not been sufficiently studied, but seems problematic, because in this case, the process would require a higher temperature (~250 °C), which would promote C–C bond cleavage (*i.e.*, depolymerization) and fluorination. Other fluorinating agents ($SF_4$, $UF_6$) are suitable only to solve particular tasks. All these circumstances and the difficulty to control the structures of the direct and plasma chemical fluorination of polymers are reasons in favour of using polymerization (polycondensation) of fluorine-containing monomers.

Some issues in this field have not been adequately explored. In many polymers considered in this review, the concentration of C–F bonds is low and effects they induce, although manifested, would be much more pronounced if the concentration of these bonds was higher. This is indicated, for example, by comparison with perfluorinated

polymers. A highly important and useful feature of fluorine-containing polymers is low tendency for plasticization under the action of organic vapours, which is reflected in lower selectivity in the separation of gas mixtures containing such impurities or highly soluble components (*e.g.*, $CO_2$). Meanwhile, published examples convincingly demonstrating these effects are scarce. Little was done in the field of atomic modelling of the structure and properties of fluorine-containing polymers. This is the challenge for future research, which would provide more in-depth understanding of the role and applications of membranes based on fluorine-containing polymers. However, now it is clear that the use of such membranes opens up the way towards flexible control over transport properties.

The review was written with financial support of the Russian Science Foundation (Project No. 18-19-00258).

## References


1. R.D.Chambers. *Fluorine in Organic Chemistry*. (Bodmin: Blackwell Publishing, 2004)
2. R.E.Banks, K.C.Lowe. *Fluorine in Medicine in the 21st Century*. (Manchester: UMIST Chemserve, 1994)
3. S.Banerjee. *Handbook of Specialty Fluorinated Polymers. Preparation, Properties, and Applications*. (Oxford: William Andrew, 2015)
4. *Modern Fluoropolymers: High Performance Polymers for Diverse Application*. (Ed. J.Scheirs). (New York: Wiley, 1997)
5. S.Ebnesajjad. *Introduction to Fluoropolymers: Materials, Technology and Applications*. (Oxford: Elsevier, 2013)
6. V.F.Cardoso, D.M.Correia, C.Ribeiro, M.M.Fernandes, S.Lanceros-Méndez. *Polymers*, **10**, 161 (2018)
7. M.G.Dhara, S.Banerjee. *Prog. Polym. Sci.*, **35**, 1022 (2010)
8. M.V.Bermeshev, P.P.Chapala. *Prog. Polym. Sci.*, **84**, 1 (2018)
9. L.W.McKeen. *Permeability Properties of Plastics and Elastomers*. (4th Ed.). (Oxford William Andrew, 2017)
10. E.Finkelshtein, M.Gringolts, M.Bermeshev, P.Chapala, Yu.Rogan. In *Membrane Materials for Gas and Vapor Separation. Synthesis and Application of Silicon-Containing Polymers*. (Eds Yu.Yampolskii, E.Finkelshtein). (Chichester: Wiley, 2017). P. 143
11. T.Masuda. *J. Polym. Sci., Part A: Polym. Chem.*, **45**, 165 (2007)
12. T.C.Merkel, I.Pinnau, R.Prabhakar, B.D.Freeman. In *Materials Science of Membranes for Gas and Vapor Separation*. (Eds Yu.Yampolskii, I.Pinnau, B.D.Freeman). (Chichester: Wiley, 2006). P. 251
13. P.Bernardo, E.Drioli, G.Golemme. *Ind. Eng. Chem. Res.*, **48**, 4638 (2009)
14. S.Mateucci, Yu.Yampolskii, B.D.Freeman, I.Pinnau. In *Materials Science of Membranes for Gas and Vapor Separation*. (Chichester: Wiley, 2006). P. 1
15. L.M.Robeson. *J. Membr. Sci.*, **62**, 165 (1991)
16. L.M.Robeson. *J. Membr. Sci.*, **320**, 390 (2008)
17. Yu.Yampolskii, L.Starannikova, N.Belov, M.Bermeshev, M.Gringolts, E.Finkelshtein. *J. Membr. Sci.*, **453**, 532 (2014)
18. A.P.Kharitonov. Doctoral Thesis in Physical and Mathematical Sciences. Institute of Problems of Chemical Physics, RAS, Chernogolovka, 2005
19. E.Jeong, T.S.Bae, S.M.Yun, S.W.Woo, Y.S.Lee. *Colloids Surf. A*, **373**, 36 (2011)
20. Z.Wang, S.Li, B.Li, W.Lai, Y.Liu, Z.Cheng, X.Liu. *J. Fluorine Chem.*, **200**, 169 (2017)
21. D.A.Syrtsova. Candidate Thesis in Chemical Sciences, A.V.Topchiev Institute of Petrochemical Synthesis, RAS, Moscow, 2001
22. A.P.Kharitonov, N.P.Piven', R.Taege, G.Ferrier. In *Sbornik Tesisov Vserocciiskoi Konferentsii 'Polimery-2004'*. (Abstracts of Reports of the All-Russian Conference 'Polymers-2004', Moscow). Vol. 1. P. 401
23. A.P.Kharitonov, R.Taegi, G.Ferrier, N.P.Piven. *Surf. Coat. Int., Part B*, **88**, 201 (2005)
24. B.Li, J.Gao, X.Wang, C.Fan, H.Wang, X.Liu. *Appl. Surf. Sci.*, **290**, 137 (2014)
25. H.He, L.Gao, X.Yang, Q.Hu, Y.Zhang, G.Chen, W.Guo. *J. Fluorine Chem.*, **151**, 32 (2013)
26. N.P.Prorokova, V.A.Istratkin, T.Y.Kumeeva, S.Y.Vavilova, A.P.Kharitonov, V.M.Bouznik. *RSC Adv.*, **5**, 44545 (2015)
27. J.M.Mohr, D.R.Paul, Y.Taru, T.E.Mlsna, R.J.Lagow. *J. Appl. Polym. Sci.*, **42**, 2509 (1991)
28. A.P.Kharitonov, Yu.L.Moskvin. *J. Fluorine Chem.*, **91**, 87 (1998)
29. M.Langsam, M.Anand, E.J.Karwacki. *Gas Sep. Purif.*, **2**, 162 (1988)
30. J.M.Mohr, D.R.Paul, I.Pinnau, W.J.Koros. *J. Membr. Sci.*, **56**, 77 (1991)
31. J.D.Le Roux, D.R.Paul, J.Kampa, R.J.Lagow. *J. Membr. Sci.*, **94**, 121 (1994)
32. J.D.Le Roux, D.R. Paul, J. Kampa, R. J.Lagow. *J. Membr. Sci.*, **90**, 21 (1994)
33. J.D.Le Roux, V.V.Teplyakov, D.R.Paul. *J. Membr. Sci.*, **90**, 55 (1994)
34. A.A.Pud, S.P.Rogalsky, G.S.Shapoval, A.P.Kharitonov, V.V.Teplyakov, H.Strathman. *Polymer*, **42**, 1907 (2001)
35. S.A.Lee, S.H.Oh, W.Lee. *J. Colloid Interface Sci.*, **332**, 461 (2009)
36. Z.Zhu, Y.Xia, G.Niu, J.Liu, C.Wang, H.Jiang. *Wear*, **376**, 1314 (2017)
37. A.V.Maksimkin, F.S.Senatov, V.D.Danilov, K.S.Mostovaya, S.D.Kaloshkin, M.V.Gorshenkov, A.P.Kharitonov, D.I.Chukov. *Mendeleev Commun.*, **26**, 350 (2016)
38. J.Peyroux, M.Dubois, E.Tomasella, N.Batisse, A.Kharitonov, D.Flahaut, L.Romana, P.Thomas. *Surf. Coat. Technol.*, **292**, 144 (2016)
39. A.P.Kharitonov, G.V.Simbirtseva, V.G.Nazarov, V.P.Stolyarov, M.Dubois, J.Peyroux. *Prog. Org. Coat.*, **88**, 127 (2015)
40. J.Peyroux, M.Dubois, E.Tomasella, L.Frézet, A.Kharitonov, D.Flahaut. *Eur. Polym. J.*, **66**, 18 (2015)
41. A.P.Kharitonov, R.Taege, G.Ferrier, V.V.Teplyakov, D.A.Syrtsova, G.H.Koops. *J. Fluorine Chem.*, **126**, 251 (2005)
42. A.P.Kharitonov, L.N.Kharitonova, Yu.L.Moskvin, V.V.Teplyakov, D.A.Syrtsova, G.H.Koops, A.J.B.Kempreman, R.P.Singh. *Int. J. Plast. Technol.*, **6**, 37 (2003)
43. Y.W.Fei, H.Q.Tang, H.W.Yang, L.P.Tong. *Contemp. Chem. Ind.*, **9**, 012 (2011)
44. H.W.Yang, Y.W.Fei, Y.Li, C.Wu, S.L.Yang. *Packag. Eng.*, **13**, 040 (2010)
45. J.Friedrich. *The Plasma Chemistry of Polymer Surfaces: Advanced Techniques for Surface Design*. (Weinheim: Wiley-VCH, 2012)
46. A.Fridman. *Plasma Chemistry*. (Cambridge: Cambridge University Press, 2008)
47. T.Yasuda, T.Okuno, K.Yoshida, H.Yasuda. *J. Polym. Sci., Part B: Polym. Phys.*, **26**, 1781 (1988)
48. X.Wei, B.Zhao, X.-M.Li, Z.Wang, B.-Q.Hec, T.He, B.Jiang. *J. Membr. Sci.*, **407 – 408**, 164 (2012)
49. A.Tressaud, E.Durand, C.Labrugère, A.P.Kharitonov, L.N.Kharitonova *J. Fluorine Chem.*, **128**, 378 (2007)
50. S.S.Borisov, V.S.Khotimsky, A.I.Rebrov, S.V.Rykov, D.I.Slovetsky, Yu.M.Pashunin. *J. Membr. Sci.*, **125**, 319 (1997)
51. F.Huber, J.Springer, M.Muhler. *J. Appl. Polym. Sci.*, **63**, 1517 (1997)

52. E.M.Kennedy, S.K.Kundu, J.C.Mackie, C.I.Holdsworth, T.S.Molloy, V.V.Gaikwad, B.Z.Dlugogorski. *Ind. Eng. Chem. Res.*, **51**, 11279 (2012)
53. W.-I.Sohn, J.-K.Koo, S.-J.Oh. *Korean J. Chem. Eng.*, **17**, 678 (2000)
54. I.Muzammil, Y.Li, M.Lei. *Plasma Proc. Polym.*, **14**, e1700053 (2017)
55. I.Muzammil, Y.P.Li, X.Y.Li, M.K.Lei. *Appl. Surf. Sci.*, **436**, 411 (2017)
56. A.Milella, F.Palumbo,P.Favia,G.Cicala, R.d'Agostino. *Plasma Proc. Polym.*, **1**, 164 (2004)
57. J.Lee, K.-J.Kim, Y.Lee. *J. Surf. Anal.*, **17**, 269 (2011)
58. J.Huberta, J.Mertensa, T.Dufoura, N.Vandencasteelea, F.Reniersa, P.Vivilleb, R.Lazzaronib, M.Raes, H.Terryn. *J. Mater. Res.*, **30**, 3177 (2015)
59. S.-J.Oh, W.P.Zurawsky. *J. Membr. Sci.*, **120**, 89 (1996)
60. S.Kirk, M.Strobel, C.-Y.Lee, S.J.Pachuta, M.Prokosch, H.Lechuga, M.E.Jones, C.S.Lyons, S.Degner, Y.Yang, M.J.Kushner. *Plasma Proc. Polym.*, **7**, 107 (2010)
61. J.A.Franco, S.E.Kentish, J.M.Perera, G.W.Stevens. *Ind. Eng. Chem. Res.*, **50**, 4011 (2011)
62. G.da Silva Padilha, V.Mansanares, J.R.Bartoli. *Polímeros*, **23**, 585 (2013)
63. N.Inagaki. *J. Membr. Sci.*, **27**, 63 (1986)
64. S.Oh, Y.Zeng, J.-K.Koo, W.P.Zurawsky. *J. Appl. Polym. Sci.*, **57**, 1277 (1995)
65. H.Kita, M.Shigekuni, K.Tanaka, K.-I.Okamoto, I.Kawafune. *J. Photopolym. Sci. Technol.*, **8**, 385 (1992)
66. Yu.P.Yampolskii, A.M.Polyakov, A.Yu.Alentiev. *Polym. Sci., A*, **47**, 885 (2005)
67. I.Gancarz, M.Bryjak, J.Kujawski, J.Wolska, J.Kujawa. *Mater. Chem. Phys.*, **151**, 233 (2015)
68. M.Li, W.Wang, K.Teng, Z.Xu, C.Li, M.Shan, C.Yang, X.Qian, X.Jiao. *J. Nanosci. Nanotechnol.*, **17**, 8935 (2017)
69. M.Tian, Y.Yin, C.Yang, B.Zhao, J.Song, J.Liu, X.M.Li, T.He. *Desalination*, **369**, 105 (2015)
70. V.F.Cardoso, D.M.Correia, C.Ribeiro, M.M.Fernandes, S.Lanceros-Méndez. *Polymers*, **10**, 161 (2018)
71. L.C.Clark, F.Gollan. *Science*, **152**, 1755 (1966)
72. A.Alentiev, Yu.Yampolskii, V.Ryzhikh, D.Tsarev. *Petrol. Chem.*, **53**, 554 (2013)
73. K.Tanaka, K.-I.Okamoto. In *Materials Science of Membranes for Gas and Vapor Separation*. (Eds Yu.Yampolskii, I.Pinnau, B.D.Freeman). (Chichester: Wiley, 2006). P. 271
74. W.J.Koros, D.R.B.Walker. *Polym. J.*, **23**, 481 (1991)
75. K.Tanaka, H.Kita, M.Okano, K.Okamoto. *Polymer*, **33**, 585 (1992)
76. J.-H.Kim, S.-B.Lee, S.Y.Kim. *J. Appl. Polym. Sci.*, **77**, 2756 (2000)
77. Y.Hirayama, T.Yoshinaga, Y.Kusuki, K.Ninomiya, T.Sakakibara, T.Tamari. *J. Membr. Sci.*, **111**, 169 (1996)
78. S.Matsui, T.Nakagawa. *J. Appl. Polym. Sci.*, **67**, 49 (1998)
79. K.Tanaka, M.Okano, H.Kita, K.Okamoto, S.Nishi. *Polym. J.*, **26**, 1186 (1994)
80. C.S.Bickel, W.J.Koros. *J. Membr. Sci.*, **170**, 205 (2000)
81. A.Shimazu, T.Miyazaki, M.Maeda, K.Ikeda. *J. Polym. Sci., Part B: Polym. Phys. Ed.*, **38**, 2525 (2000)
82. M.Al-Masri, H.R.Kricheldorf, D.Fritsch. *Macromolecules*, **32**, 7853 (1999)
83. B.Dasgupta, S. K.Sen, S.Banerjee. *J. Membr. Sci.*, **345**, 249 (2009)
84. S.Japip, K.-S.Liao, Y.Xiao, T.-S.Chung. *J. Membr. Sci.*, **497**, 248 (2016)
85. S.K.Sen, B.Dasgupta, S.Banerjee. *J. Membr. Sci.*, **343**, 97 (2009)
86. S.K.Sen, S.Banerjee. *J. Membr. Sci.*, **365**, 329 (2010)
87. S.K.Sen, S.Banerjee. *J. Membr. Sci.*, **350**, 53 (2010)
88. S.K.Sen, S.Banerjee. *RSC Adv.*, **2**, 6274 (2012)
89. S.Ghosh, S.Banerjee. *J. Membr. Sci.*, **497**, 172 (2016)
90. T.Koley, P.Bandyopadhyay, A.K.Mohanty, S.Banerjee. *Eur. Polym. J.*, **49**, 4212 (2013)
91. H.Gao, D.Wang, W.Jiang, S.Guan, Z.Jiang. *J. Appl. Polym. Sci.*, **109**, 2341 (2008)
92. D.Bera, P.Bandyopadhyay, S.Ghosh, S.Banerjee, V.Padmanabhan. *J. Membr. Sci.*, **474**, 20 (2015)
93. D.Bera, V.Padmanabhan, S.Banerjee. *Macromolecules*, **48**, 4541 (2015)
94. S.Bisoi, A.K.Mandal, V.Padmanabhan, S.Banerjee. *J. Membr. Sci.*, **522**, 77 (2017)
95. S.Bisoi, P.Bandyopadhyay, D.Bera, S.Banerjee. *Eur. Polym. J.*, **66**, 419 (2015)
96. D.Bera, P.Bandyopadhyay, S.Ghosh, S.Banerjee. *J. Membr. Sci.*, **453**, 175 (2014)
97. P.Bandyopadhyay, D.Bera, S.Ghosh, S.Banerjee. *J. Membr. Sci.*, **447**, 413 (2013)
98. P.Bandyopadhyay, S.Banerjee. *Eur. Polym. J.*, **69**, 140 (2015)
99. P.Bandyopadhyay, D.Bera, S.Ghosh, S.Banerjee. *RSC Adv.*, **4**, 28078 (2014)
100. D.Bera, P.Bandyopadhyay, B.Dasgupta, S.Banerjee. *J. Membr. Sci.*, **407–408**, 116 (2012)
101. J.M.Mohr, D.R.Paul, G.L.Tullos, P.E.Cassidy. *Polymer*, **32**, 2387 (1991)
102. Z.Xu, C.Dannenberg, J.Springer, S.Banerjee, G.Maier. *J. Membr. Sci.*, **205**, 23 (2002)
103. M.R.Pixton, D.R.Paul. *J. Polym. Sci., Part B: Polym. Phys.*, **33**, 1135 (1995)
104. Z.Xu, C.Dannenberg, J.Springer, S.Banerjee, G.Maier. *Chem. Mater.*, **14**, 3271 (2002)
105. S.Banerjee, G.Maier, C.Dannenberg, J.Spinger. *J. Membr. Sci.*, **229**, 63 (2004)
106. W.Y.Huang, B.R.Liaw, M.Y.Chang, Y.K.Han, P.T.Huang. *Macromolecules*, **40**, 8649 (2007)
107. I.M.Tkachenko, N.A.Belov, Yu.V.Yakovlev, P.V.Vakuliuk, O.V.Shekera, Yu.P.Yampolskii, V.V.Shevchenko. *Mater. Chem. Phys.*, **183**, 279 (2016)
108. S.Ghosh, S.Banerjee. *J. Membr. Sci.*, **470**, 535 (2014)
109. S.Ghosh, D.Bera, P.Bandyopadhyay, S.Banerjee. *Eur. Polym. J.*, **52**, 207 (2014)
110. I.Tkachenko, N.Belov, Yu.Kobzar, A.Dorokhin, O.Shekera, V.Shantarovich, V.Bekeshev, V.Shevchenko. *J. Fluorine Chem.*, **195**, 1 (2017)
111. L.K.Xu, M.Bohning, J.Springer, N.Steinhauser, R.Mulhaupt. *Polymer*, **38**, 581 (1997)
112. S.Makhseed, J.Samuel, A.Bumajdada, M.Hassan. *J. Appl. Polym. Sci.*, **109**, 2591 (2008)
113. I.Tkachenko, Ya.Kobzar', O.Shekera, V.Shevchenko. *Polimer. Zh.*, **40** (2), 93 (2018)
114. Y.Xiao, L.Zhang, L.Xu, T.-S.Chung. *J. Membr. Sci.*, **521**, 65 (2017)
115. M.Lee, C.G.Bezzu, M.Carta, P.Bernardo, G.Clarizia, J.C.Jansen, N.B.McKeown. *Macromolecules*, **49**, 4147 (2016)
116. K.Nagai, T.Masuda, T.Nakagawa, B.D.Freeman, I.Pinnau. *Prog. Polym. Sci.*, **26**, 721 (2001)
117. T.Sakaguchi, Y.Hu, T.Masuda. In *Membrane Materials for Gas and Vapor Separation. Synthesis and Application of Silicon Containing Polymers*. (Eds Yu.Yampolskii, E.Finkelshtein). (Chichester: Wiley, 2017). P. 107
118. T.Masuda, K.Nagai. In *Materials Science of Membranes for Gas and Vapor Separation*. (Eds Yu.Yampolskii, I.Pinnau, B.D.Freeman). (Chichester: Wiley, 2006). P. 231
119. T.Sakaguchi, M.Shiotsuki, F.Sanda, B.D.Freeman, T.Masuda. *Macromolecules*, **38**, 8327 (2005)
120. A.Fukui, K.Hattori, M.Shiotsuki, F.Sanda, T.Masuda. *Polymer*, **50**, 4159 (2009)
121. Y.Hayakawa, M.Nishida, T.Aoki, H.Muramatsu. *J. Polym. Sci., Part A: Polym. Chem. Ed.*, **30**, 873 (1992)
122. K.Tsuchihara, T.Masuda, T.Higashimura, M.Nishida, H.Muramatsu. *Polym. Bull.*, **23**, 505 (1990)

123. T.Masuda, Y.Iguchi, B.-Z.Tang, T.Higashimura. *Polymer*, **29**, 2041 (1988)
124. T.Sato, N.Yoshida, A.Ishida, M.Teraguchi, T.Aoki, T.Kaneko. *Polymer*, **54**, 2231 (2013)
125. Y.Hu, M.Shiotsuki, F.Sanda, B.D.Freeman, T.Masuda. *Macromolecules*, **41**, 8525 (2008)
126. A.Kossov, V.Khotimskiy. *Polymer*, **55**, 989 (2014)
127. Yu.Yampolskii. In *Comprehensive Membrane Science and Technology*. Vol. 1. (Eds E.Drioli, L.Giorno). (Elsevier, 2010). P. 131
128. E.Sh.Finkelshtein, M.V.Bermeshev, M.L.Gringolts, L.E.Starannikova, Yu.P.Yampolskii. *Russ. Chem. Rev.*, **80**, 341 (2011)
129. V.V.Teplyakov, D.R.Paul, N.B.Bespalova. *Macromolecules*, **25**, 4218 (1992)
130. Yu.Yampolskii, N.Bespalova, E.Finkelshtein, V.Bondar, A.Popov. *Macromolecules*, **27**, 2872 (1994)
131. M.A.Tlenkopatchev, J.Vargas, M.A.Girøn, M.Lípez-Gonzôlez, E.Riande. *Macromolecules*, **38**, 2696 (2005)
132. A.A.Santiago, J.Vargas, R.Gavino, A.M.Cerda, M.A.Tlenkopatchev. *Macromol. Chem. Phys.*, **208**, 1085 (2007)
133. J.Vargas, A.Martınez, A.A.Santiago, M.A.Tlenkopatchev, M.Aguilar-Vega. *Polymer*, **48**, 6546 (2007)
134. J.Vargas, A.Martinez, A.A.Santiago, M.A.Tlenkopatchev, R.Gaviso, M.Aguilar-Vega. *J. Fluorine Chem.*, **130**, 162 (2009)
135. J.Vargas, A.A.Santiago, M.A.Tlenkopatchev, M.Lopez-Gonzalez, E.Riande. *J. Membr. Sci.*, **361**, 78 (2010)
136. J.A.Cruz-Morales, J.Vargas, A.A.Santiago, S.R.Vasquez-Garcia, M.A.Tlenkopatchev, T.de Lys, M.Lopez-Gonzalez. *High Perform. Polym.*, **28**, 1246 (2016)
137. 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.Sh.Finkelshtein. *Polymer*, **153**, 626 (2018)
138. M.Bermeshev, L.Starannikova, S.Sterlin, A.Tyutyunov, A.Tavtorkin, Yu.Yampolskii, E.Finkelshtein. *Petrol. Chem.*, **55**, 753 (2015)
139. A.A.Morontsev, V.A.Zhigarev, R.Yu.Nikiforov, N.A.Belov, M.L.Gringolts, E.Sh.Finkelshtein, Yu.P.Yampolskii. *Eur. Polym. J.*, **99**, 340 (2018)
140. T.Huang, J.M.Messman, J.W.Mays. *Macromolecules*, **41**, 266 (2008)
141. A.C.Puleo, N.Muruganandam, D.R.Paul. *J. Polym. Sci., Part B: Polym. Phys.*, **27**, 2385 (1989)
142. V.S.Khotimskii, V.G.Filippova, I.S.Bryantseva, V.I.Bondar, V.P.Shantarovich, Yu.P.Yampolskii. *J. Appl. Polym. Sci.*, **78**, 1612 (2000)
143. N.A.Belov, R.Yu.Nikiforov, M.V.Bermeshev, Yu.P.Yampolskii, E.Sh.Finkelshtein. *Membr. Membr. Technol.*, **7**, 305 (2017)
144. F.Z.Khan, T.Sakaguchi, M.Shiotsuki, Y.Nishio, T.Masuda. *Macromolecules*, **39**, 9208 (2006)
145. Z.Cui, E.Drioli, Y.M.Lee. *Prog. Polym. Sci.*, **39**, 164 (2014)
146. R.A.Pasternak, M.V.Christensen, J.Heller. *Macromolecules*, **3**, 366 (1970)
147. M.Yavari, Y.Okamoto, H.Lin. *J. Membr. Sci.*, **548**, 380 (2018)
148. R.Nikiforov, N.Belov, A.Zharov, I.Konovalova, B.Shklyaruk, Yu.Yampolskii. *J. Membr. Sci.*, **540**, 129 (2017)
149. *Membrane Distillation: Basic Aspects and Applications. J. Membr. Sci., Virtual Spec. Issue 2012*. (Eds E.Drioli, F.Macedonio, A.Ali); http://www.journals.elsevier.com/journalof-membrane-science/virtual-special-issues/membrane-distillation-basic-aspects-and-applications
150. E.Drioli, A.Criscuoli, E.Curcio. In *Membrane Science and Technology Series*. Vol. 11. (Eds M.Wessing, K.Sirkar). (Amsterdam: Elsevier, 2006). P. 502
151. M.S.Khayet, T.Matsuura. *Membrane Distillation: Principles and Applications*. (Amsterdam: Elsevier, 2010)
152. E.Drioli, G.Di.Profio, E.Curcio. *Curr. Opin. Chem. Eng.*, **1**, 1 (2012)
153. G.Belfort, R.H.Davis, A.L.Zydney. *J. Membr. Sci.*, **96**, 1 (1994)
154. Patent US 5051114 (1991)
155. Patent US 5883177 (1999)
156. B.C.H.Steele, A.Heinzel. *Nature (London)*, **414**, 345 (2001)
157. K.A.Mauritz, R.B.Moore. *Chem. Rev.*, **104**, 4535 (2004)
158. I.Pinnau, L.G.Toy. *J. Membr. Sci*, **109**, 125 (1996)
159. A.Yu.Alentiev, Yu.P.Yampolskii, V.P.Shantarovich, S.M.Nemser, N.A.Plate. *J. Membr. Sci.*, **126**, 123 (1997)
160. M.Fang, Z.He, T.C.Merkel, Y.Okamoto. *J. Mater. Chem., A*, **6**, 652 (2018)
161. Patent US 5902747 (1999)
162. S.M.Nemser. In *Proceedings of the 16th Annual Membrane Technology Separation Planning Conferense, Newton, MA*, 1998
163. A.Yu.Alentiev, N.A.Belov, R.Yu.Nikiforov, E.V.Polunin, N.V.Borovkova, M.S.Makarov, M.V.Storozheva, A.K.Evseev, I.V.Goncharovskaya, S.V.Zhuravel'. *Membr. Membr. Technol.*, **8**, 217 (2018)
164. A.M.Polyakov, L.E.Starannikova, Yu.P.Yampolskii. *J. Membr. Sci.*, **216**, 2416 (2003)
165. J.Chau, P.Basak, K.K.Sirkar. *J. Membr. Sci.*, **563**, 541 (2018)