 © 2016 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RCR4546

Membrane materials based on polyheteroarylenes and their application for pervaporation

A Yu Pulyalina, G A Polotskaya, A M Toikka

Saint Petersburg State University
Universitetskaya nab. 7/9, 199034 St Petersburg, Russian Federation

Studies on the transport properties of membrane materials are topical in connection with the need to solve the fundamental problems and to analyze the applied aspects of the theory of membrane separation processes including, in particular, the development of the energy- and resource-saving, environmentally safe technologies. The aim of the review is to generalize the experimental data on the separation of practically valuable mixtures using membranes based on polyheteroarylenes (thermally stable and mechanically strong polymers). First of all, our analysis covers publications that give a detailed description of the physicochemical properties of the membranes and an interpretation of the specific features of mass transfer during pervaporation of liquid mixtures using membrane materials based on polyheteroarylenes. The dependences of the transport parameters of pervaporation on the process conditions and on the methods for production of membrane materials are discussed. The data presented may be useful for the development of the theory of membrane processes taking into account the chemical nature and physicochemical features of polymeric membrane materials.
The bibliography includes 151 references.

Contents

I. Introduction 81
II. Pervaporation, challenges and opportunities 82
III. Polyheteroarylenes as membrane materials 84
IV. Dehydration of organic solvents 87
V. Removal of organics from water 91
VI. Separation of organic liquid mixtures 92
VII. Conclusion 96

I. Introduction

Intensification of membrane separation processes belongs to key problems in modern basic research and applied studies on membrane technologies. Three lines of research activity aimed at solving the problem include the design of advanced membrane materials as well as new types of membrane modules and processes (hybrid, composite ones, *etc.*).[1–6] Undoubtedly, the role of the membrane material is of paramount importance, although in some particular cases the conditions for transmembrane mass transfer can to some extent influence its efficiency. Traditionally, membrane processes are classified as crucially important energy- and resource-conserving, environmentally safe technologies,[1–3] including the design of coupled processes, *e.g.*, in the case of membrane contactors[7,8] or absorbing pervaporation.[9]

A membrane is a structure, having lateral dimensions much greater than its thickness, through which transfer may occur under a variety of driving forces (IUPAC, 1996).[10] Practically, the emphasis should be placed on the membrane materials that ensure the highest efficiency of separation.[11,12] The most important class of membrane materials includes organic polymers, the choice of a particular polymer being dependent on its structure and properties.[12] A polymer can be used to prepare membranes of different morphology (structure). The morphology specifies the mechanism of separation and, therefore, the application fields of the membranes.

Nonporous membranes occupy a particular position. Mass transfer through these systems is described by the solution – diffusion model. Compared to porous membranes, the diffusion mechanism provides a stronger interaction of molecules of the liquids being separated with the

A Yu Pulyalina PhD, Senior Lecturer of the Department of Chemical Thermodynamics and Kinetics at the Institute of Chemistry, SPbSU. Telephone: +7 (812) 428 – 4805, e-mail: a.pulyalina@spbu.ru
Current research interests: membrane processes, polymeric materials, sorption, diffusion, mass transfer through nonporous materials.
G A Polotskaya PhD, Senior Researcher of the same Department. Telephone: +7 (812) 323 – 5963, e-mail: g.polotskaya@spbu.ru
Current research interests: nanocomposites, polymers, polymeric membranes, pervaporation, mass transfer, sorption.
A M Toikka Doctor of Science, Professor, Head of the same Department. Telephone: +7 (812) 428 – 4052, e-mail: a.toikka@spbu.ru
Current research interests: general thermodynamics, chemical thermodynamics, nonequilibrium thermodynamics, phase processes, membrane processes, functional materials.

Received 2 December 2014
Uspekhi Khimii **85** (1) 81 – 98 (2016); translated by A M Raevskiy

membrane material; this allows one to separate substances with similar physical properties and chemical nature. Correspondingly, the search for efficient polymeric membrane materials is a priority investigation line in the design of technologies using diffusion membranes, in particular, for pervaporation and gas separation.

In this review we will consider membranes based on polyheteroarylenes. The transport and physicochemical properties of such systems have been intensively studied; however, only a few reviews on the title subject have been reported in the last decade.[13,14] Great prospects for application of these membranes for separation of liquid mixtures are, in particular, due to the fact that heteroaromatic polymers exhibit high stress–strain properties, thermal stability, chemical stability and the ability to change their morphology under the action of external factors or upon modification. We will restrict ourselves to a number of examples related to evaporation through nonporous polymeric membranes, *i.e.*, pervaporation.

II. Pervaporation, challenges and opportunities

The term 'pervaporation' is used in both technology and basic research to denote evaporation through a membrane. Although having a clear etymology (permeation + evaporation), it incompletely characterizes the essence of the process. Indeed, at present the notion 'pervaporation' covers a rather wide range of processes using both nonporous and porous polymeric and inorganic materials. The physicochemical laws of the process conducted using fundamentally different types of membranes are significantly different. However, polymeric membranes remain the most abundant class of pervaporation membranes; therefore, in this review 'pervaporation' means evaporation through a nonporous polymeric membrane.

Pioneering laboratory and applied pervaporation studies date back to the early 20th century. The term 'pervaporation' was coined by Kober.[15] Since then, research into pervaporation was mainly of academic interest despite the fact that problems in most studies were initially posed as applied ones. The process has been industrially and commercially used since 1982. At that time, the first pilot plant for dehydration of ethanol was put in operation by the German company GFT in Brasil.[16] Progress in pervaporation studies and technological applications of the process are well documented in monographs and reviews.[1,2,17–19]

As to the recent studies, original communications on pervaporation represent a large proportion of publications devoted to membrane processes. Since 2004, more than 350 articles concerning various aspects of pervaporation process have been published only in such a recognized journal as the *Journal of Membrane Science*. Earlier, patents and original publications on membrane methods of separation including pervaporation were analyzed by, *e.g.*, Semenova and coworkers,[20,21] in a collective monograph [1] and in a number of reviews.[22–24]

As mentioned above, the solution–diffusion mechanism of transmembrane transfer during pervaporation remains the most commonly accepted.[2] Two regimes of the process are recognized, *viz.*, vacuum-driven pervaporation and carrier-gas pervaporation (in the latter case, gaseous product is removed from the system with a flow of 'inert' carrier gas); however, the vast majority of applied pervaporation studies deal with the vacuum-driven process (Fig. 1).

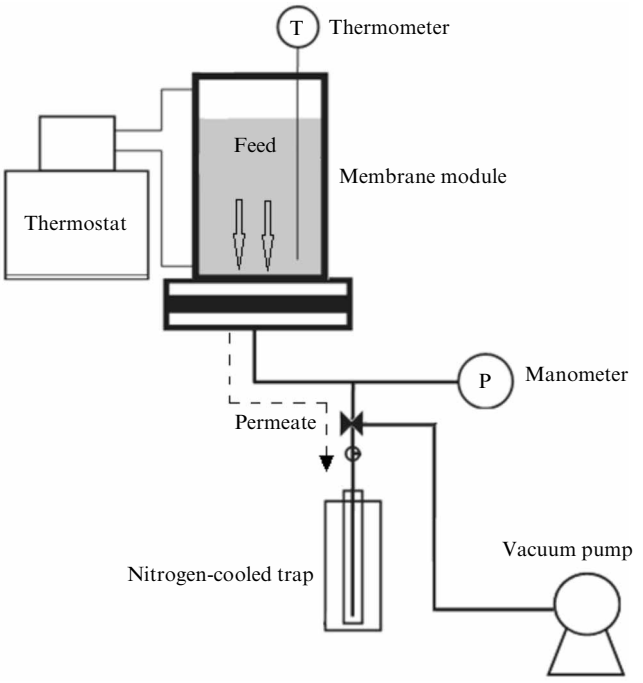


Figure 1. Vacuum-driven pervaporation: a schematic.

According to the solution–diffusion mechanism, separation is achieved through preferred sorption and dissolution of particular components of a mixture by the membrane material and owing to different diffusion rate of the substances being separated across the membrane. Particular stages of the process (sorption + dissolution and diffusion) can either exhibit synergistic effect or compete, acting in opposite directions. For instance, a certain component of a mixture can be well soluble in the membrane material, but a low rate of its diffusion can influence the course of the overall separation process.

The process completes with desorption. Generally, transmembrane mass transfer can result in gaseous or liquid products. In the case of vacuum- or carrier-gas driven desorption, one deals with gaseous permeates. Therefore, at first glance, the term 'evaporation' is conditional because it in essence characterizes only the sampling method of permeates. At the same time, in the case of nonporous polymeric membranes the process is driven just by the pressure drop from atmospheric pressure to a vacuum; as a consequence, products of transmembrane transfer are in the vapour phase, *i.e.*, in almost all cases one should speak of evaporation through a membrane.

In the vacuum-driven regime, evaporation through a nonporous membrane is due to the pressure drop (pressure difference between different sides of the membrane).[5] In addition, it is often pointed out that the process is driven by the chemical potential difference between the feed mixture and product. Although thermodynamically attractive, this interpretation seems to be incorrect just from the thermodynamic point of view. Indeed, the pervaporation product is immediately removed and, therefore, its contribution (chemical potentials of components μ_i) to the driving force of the process is negligible. Recall that in accordance with the expression for the chemical potential, if the partial

pressure or concentration of a component tends to zero, the chemical potential of the component tends to $-\infty$:

$$\mu_i = \mu_i^{\circ}(T) + RT\ln p_i$$

where $\mu_i^{\circ}(T)$ is the standard chemical potential μ_i equal to the chemical potential of the pure substance i at temperature T; R is the universal gas constant; and p_i is the partial pressure. A similar situation is observed in the simple case of open equilibrium evaporation from a free surface (no membrane), where the relative concentrations of components in the vapour (and corresponding relative evaporation rates) are determined by their partial pressures, *i.e.*, the chemical potentials of components in the liquid phase rather than by the μ_i difference between the liquid and vapour phases. In both cases, *i.e.*, evaporation through a membrane or with no membrane, one deals with an open phase process which is by default characterized by continuous removal of the phase being formed.[25,26]

The partial pressures of components of the feed can undoubtedly be included in the estimation of the selectivity and fluxes in the case of evaporation through a nonporous membrane as the thermodynamic parameters of the components; however, sorption + dissolution and diffusion are at least equally important stages of the process. This is just a significant difference between evaporation from free surface and evaporation through a membrane.

Some authors admit the occurrence of a vapour–liquid phase transition during pervaporation prior to the sorption step.[5,27] Since, in contrast to related processes (gas separation and vapour separation), the solution contacts the membrane surface during pervaporation, the inclusion of this phase transition to the mechanism seems to be a theoretical admission rather than an actual step of the process. If evaporation does precede the sorption and dissolution steps, the partial pressures (p_i) of components of the feed should play a significant role because it is these parameters that govern the concentrations of substances in the vapour formed (before sorption).

A number of authors compared gas (vapour) separation and pervaporation (see, *e.g.*, Refs 2 and 28–30). Considering these processes, Baker,[2] in particular, points to numerous experimental studies whose authors report that transmembrane mass transfer from the liquid is faster but less selective than mass transfer from the equilibrium vapour. Baker treated these results as experimental artifacts, emphasized that during vapour separation the vapour contacting the membrane is not completely saturated, and concluded that the activities of the feed components in vapour separation experiments are lower than in pervaporation experiments. As a result, the conclusion that the vapour fluxes are lower than the pervaporation fluxes is substantiated only by high sensitivity of the sorption by the membrane materials to activity. We believe that such a comparative analysis of the efficiency of two membrane processes seems to be far from being comprehensive in spite of the use of thermodynamic concepts. Complicated processes like pervaporation and gas (vapour) separation are strongly influenced by not only activities of components, but also the properties of the membrane material, the concentration polarization as well as by swelling, heat effects, total pressure gradients, *etc.*

Thermodynamically, vacuum-driven evaporation through a membrane should be treated as nonequilibrium process and, therefore, analyzed using the formalism of nonequilibrium thermodynamics. A membrane system represents a classical example of a discontinuous system;[31–33] the notions 'membrane system' and 'discontinuous system' can be considered identical. Although mass transfer through nonporous membranes differs from, *e.g.*, mass transfer through porous membranes, capillaries and other types of barriers between compartments of a discontinuous system, thermodynamic description of all these systems is of the same type.

When pervaporation and other membrane processes are analyzed using the formalism of nonequilibrium thermodynamics, one can use linear laws (phenomenological equations), although generally, linear relationships between flows and thermodynamic forces exist only in the vicinity of equilibrium state.[34] For instance, the relationships for two pairs of flows and forces are described by the system of equations (1):

$$\left.\begin{aligned} J_1 &= L_{11}X_1 + L_{12}X_2 \\ J_2 &= L_{21}X_1 + L_{22}X_2 \end{aligned}\right\} \quad (1)$$

where L_{ii} and L_{ik} are the direct and cross phenomenological coefficients, J_i is the flow of the property i, X_i is the conjugate thermodynamic force (in our case, only one component of the vectors of the corresponding flows and forces). For diffusion during the transmembrane transport the coefficients L_{ii} and L_{ik} are some quantities proportional to the diffusion coefficients. Although the phenomenological equations (1) are not thermodynamic relations (linear relations appear in extended thermodynamics), there exist some thermodynamic limitations. Since the entropy production is non-negative [34]

$$\sigma = \sum_{i,k} L_{ik}X_iX_k \geqslant 0 \quad (2)$$

where σ is the local entropy production, '$>$' corresponds to nonequilibrium processes, and '$=$' corresponds to equilibrium ones, the matrix of kinetic coefficients should be positive-definite. Other limitations are due to the symmetry condition for the matrix of kinetic coefficients, *viz.*, $L_{ik} = L_{ki}$ (Onsager reciprocal relations, temporal symmetry of the system), and to the Curie principle (spatial symmetry).[34] Although coupling effects (classical case for the nonequilibrium theory) were considered even in an early thermodynamic analysis of pervaporation by Kedem,[35] only a few studies on pervaporation and other membrane processes based on the formalism of nonequilibrium thermodynamics have been reported in the last decade (see, *e.g.*, Refs 36–39).

Various modern models for the description and analysis of pervaporation are also based on general theories of membrane processes and on the approaches that characterize the specific features of evaporation through a nonporous membrane. Both particular stages (sorption, diffusion) and the overall processes are considered. Probably, a key trend in theory is an analysis using the Maxwell–Stefan equations derived as early as the 19th century.[40,41] Pioneering studies by Heintz and Stephan,[42,43] who applied these equations to evaporation through a nonporous membrane were continued by other authors (see, *e.g.*, Refs 44 and 45).

Other models for the description of membrane transport during pervaporation are based on the Fick law, the

Flory–Huggins theory, theory of free volume, on kinetic models and on the pore flow model.[46–56] One of the most recent reviews of pervaporation models is available in a collective monograph.[1]

Pervaporation membranes are characterized by the permeate flux and the separation factor. The permeate flux (kg m^{-2} h^{-1}) is the amount of a permeate per unit membrane surface per unit time. The separation factor (selectivity, α_{pv}) is a key parameter characterizing the separation properties of pervaporation membranes,

$$\alpha_{pv} = \frac{y_i/y_k}{x_i/x_k} \quad (3)$$

where y_i, y_k and x_i, x_k are the mole fractions (or mass fractions) of the substances i and k in the permeate and in the feed (solution), respectively. Clearly, Eqn (3) matches the definition of the relative volatility (α_{vl}) which characterizes the selectivity in the case of equilibrium liquid–vapour phase transition,

$$\alpha_{vl} = \frac{y_i^{(v)}/y_k^{(v)}}{x_i/x_k} \quad (4)$$

where $y_i^{(v)}$ and $y_k^{(v)}$ are the mole (or mass) fractions of components in the equilibrium vapour. In particular, the α_{pv} and α_{vl} values make it possible to compare the selectivity of evaporation through a membrane and that of equilibrium open evaporation. An additional (either positive or negative) contribution to selectivity owing to the membrane process can be characterized by the parameter E called the 'enhancement factor'.[27]

$$E = \frac{y_i/y_k}{y_i^{(v)}/y_k^{(v)}} = \frac{\alpha_{pv}}{\alpha_{vl}} \quad (5)$$

Therefore, α_{pv} can be represented as

$$\alpha_{pv} = E\alpha_{vl} \quad (6)$$

which allows the efficiency of distillation and pervaporation to be compared directly.

Although theoretical concepts of physicochemical aspects of pervaporation are different, a great practical importance of the process for technology is commonly accepted.[1] As applied to separation of mixtures of close-boiling liquids and azeotropic mixtures, pervaporation has undoubtful advances over distillation. Important application fields of the method in pharmaceutical and food industries include purification and concentration of temperature (heating)-sensitive liquids because of very mild process conditions. Pervaporation is environmentally friendly, free from environmental pollution and undemanding to extra chemicals for conducting the process.

There are three main fields of application of pervaporation:[1,47]

— dehydration of organic solvents (alcohols, esters, *etc.*) — hydrophilic pervaporation;

— removal of organics (trichloroethylene, chloroform, dichloromethane, benzene, toluene, alcohols) from water — hydrophobic pervaporation;

— separation of organic liquid mixtures (methanol–methyl *tert*-butyl ether, methanol–dimethyl carbonate, a mixture of *p*-xylene, *m*-xylene and *o*-xylene) — organophilic pervaporation.

Dehydration of organic solvents is a classical field of application of pervaporation. Here, success is due to synergistic effect, namely, water in hydrophilic membranes is characterized by better solubility and preferred diffusion owing to smaller size of water molecules.

Dehydration and purification of alcohols also becomes of importance because a number of alcohols are used as promising alternative automotive fuels.

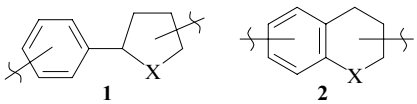
In the removal of organics dissolved in water, preferred diffusion of organic molecules is achieved using hydrophobic membranes.[1] Separation of organic mixtures ranks first among various applications of pervaporation.[57] Pervaporation separation of mixtures of polar and nonpolar liquids (*e.g.*, methanol–methyl *tert*-butyl ether), mixtures of aromatic and aliphatic liquids (benzene–n-hexane), aromatic and alicyclic liquids (benzene–cyclohexane) as well as mixtures of isomers (*e.g.*, xylene isomers) is of great industrial value. A promising and rapidly progressing field of application, namely, separation of mixtures of aromatic and aliphatic compounds (benzene–n-hexane, *etc.*), is also associated with the diffusion mechanism of transmembrane mass transfer.

In this review the emphasis is placed on the membrane materials based on polyheteroarylenes, which were recently tested in the diffusion separation of liquids using pervaporation methods in order to dehydrate of organic solvents, to remove organics from water and to separate organic liquid mixtures.

III. Polyheteroarylenes as membrane materials

Polyheteroarylenes are heteroaromatic compounds belonging to the most in-demand thermally stable, mechanically strong and chemically stable polymers. A wide variety of applications of polyheteroarylenes is, in particular, due to stepwise synthetic procedures, which imply mild conditions in the initial steps and subsequent isolation of prepolymers followed by thermal cyclization (in some cases, heat treatment of finished items). A severe drawback of this class of polymers consists in limited solubility. Processability of materials based on polyheteroarylenes can be improved in several ways, *e.g.*, by attaching bulky groups to the side chain, by synthesizing macromolecules with asymmetric structure, *etc*. However, polyheteroarylenes containing aromatic (benzene, naphthalene) carbocycles and heterocycles (imide, oxazinone, imidazole, *etc.*) in the repeating unit are of particular interest for many industries. Aromatic carbocycles can form simple bonds with heterocycles or fused to them (structures **1** and **2**).[58–60]

Structures 1, 2



1 **2**

X = N, S, O, *etc.*

Such structures can be synthesized by polymerization of monomers containing functionalized deriatives of benzene participating in the formation of a heterocycle. In the text below the emphasis is placed on polyheteroarylenes obtained in this manner.

A wide variety of properties of polyheteroarylenes is due to the structure of macromolecules and their ability to self-organization. Owing to very high thermal stability, chemical stability and radiation resistance, high mechanical strength and improved wear resistance and other specific properties of materials based on polyheteroarylenes, these polymers have found application in aviation industry, space industry, mechanical engineering, electric engineering, microelectronics and other industries.

Polyheteroarylenes belong to the most promising membrane materials because they meet all the requirements mentioned above and exhibit high operating characteristics. Unique physicochemical properties of these polymers predetermine high selectivity of separation of various mixtures. Polyheteroarylenes are used as efficient membrane materials for separation of liquid mixtures in, *e.g.*, baromembrane and electromembrane processes.[1,61–64] Owing to ordered structure, fixed free volume and appropriate thermodynamic properties, polyheteroarylenes proved themselves as materials for diffusion membrane processes where the efficiency of separation is to a great extent governed by selective transport of molecules through the polymer matrix.[65–67] Typical representatives of heteroaromatic polymers, such as polyimides, polyetherimides, polybenzimidazoles, *etc.*, are known as promising materials for gas separation[68–71] and pervaporation.[14,72]

The chemical structure of the monomer unit in polyheteroarylenes to a great extent determines the physicochemical properties of polymers and thus influences the transport properties of pervaporation membranes. This can be explained by changes in the chain flexibility, macromolecular packing, inter-chain interactions, *etc.* The physical properties of polymers are less sensitive to changes in the chemical structure than the transport properties.

Table 1 presents a list of typical representatives of membrane materials based on polyheteroarylenes. Traditionally, in scientific literature polyimides are denoted by Latin abbreviations based on the names of the dianhydride and diamine moieties or by commercial trademarks of corresponding commercial polyheteroarylenes. We also follow this tradition. Russian abbreviations were used only in the description of the polyheteroarylenes studied by the authors of this review.

One should keep in mind that particular numerical values of the transport parameters reported in original studies are often determined for different types of membranes (homogeneous films, asymmetric films, composite membranes), mixtures of somewhat different composition or are measured at different temperatures. Therefore, a direct comparison of these values is to some extent incorrect. Nevertheless, we believe that such a comparison will give a clearer picture of the transport properties of novel membrane materials based on polyheteroarylenes and demonstrate their potential in separation of various liquid mixtures.

Particular examples of application of polyheteroarylenes as materials for pervaporation membranes will be considered in Sections IV–VI.

Table 1. Polyheteroarylenes used as membrane materials.

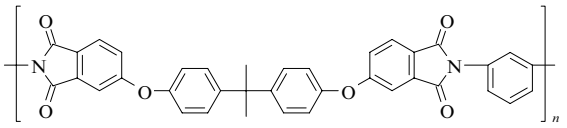
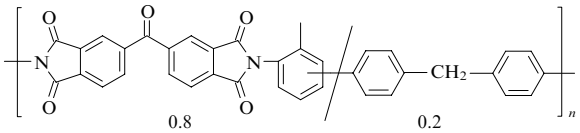
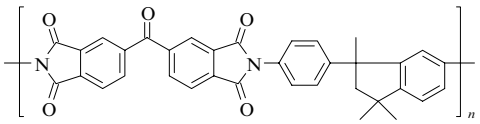
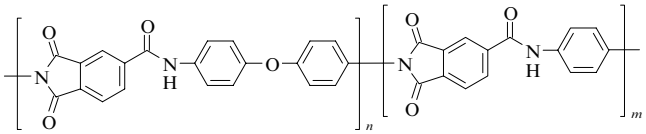
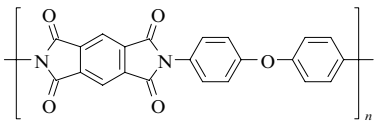
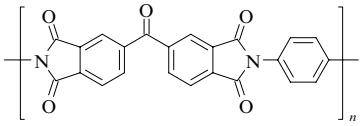
Designation	Repeating unit structure
Ultem	
P84	
Matrimid	
Torlon	
Kapton (PMDA-DA)	
BTDA-PDA	

Table 1 (continued).

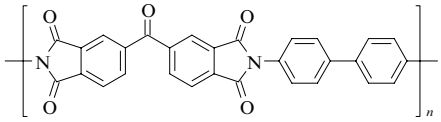
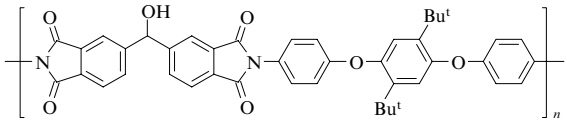
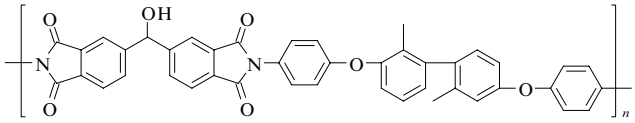
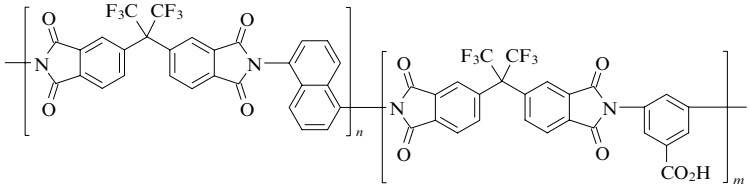
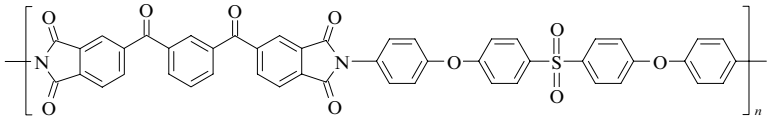
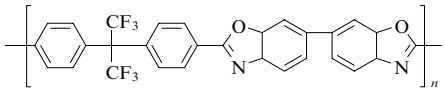
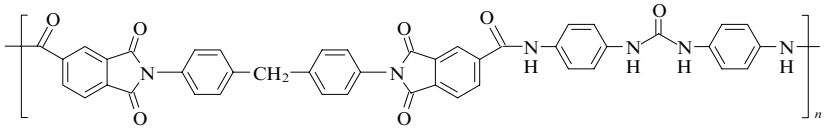
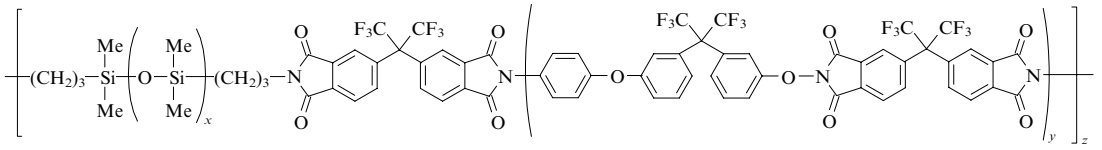
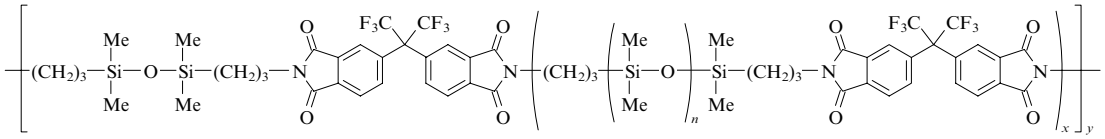
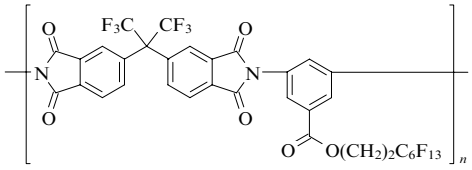
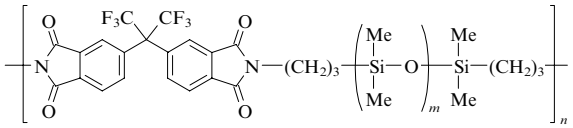
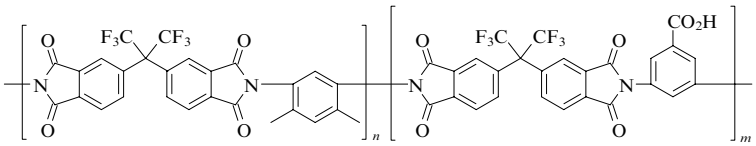
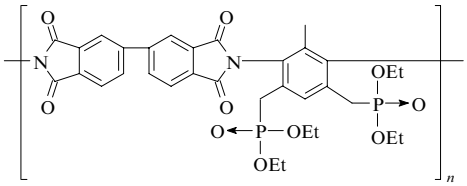
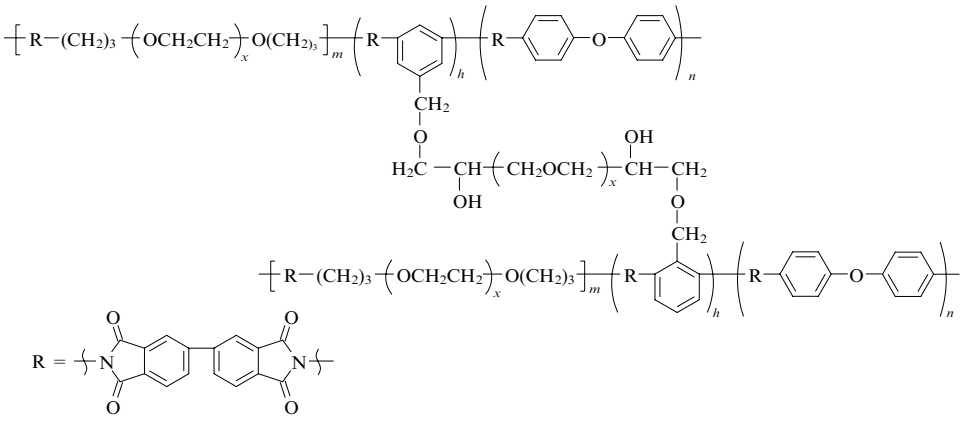
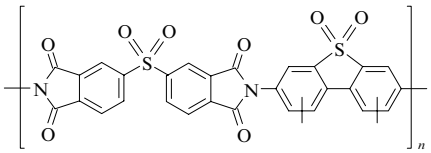
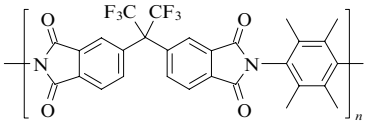
Designation	Repeating unit structure
BTDA-BZD	
BHTDA-BADTB	
BHTDA-DBAPB	
6FDA-NDA/DABA	
PEI (polyetherimide)	
PBO (polybenz-oxazole)	
PCA (polycarbamide)	
PSI-3	
PSI	
6FDA-PFDAB	
6FDA-SIDA	

Table 1 (continued).

Designation	Repeating unit structure
6FDA-DAM/DABA	
BPDA-TMPD (phosphorylated)	
PEO-PI	
DSDA-DDBT	
6FDA-MDA	

IV. Dehydration of organic solvents

Dehydration of organic solvents (alcohols, acids, ethers and ketones) belongs to the most rapidly progressing applications of pervaporation. Dehydration of alcohols has become a challenge in the 1980s where alcohols (ethanol, butanol) appeared to be on-demand as promising alternative fuels competitive with petrol on the energy market. In Americas and Europe, pure alcohols and their mixtures with petrol (3 mass % – 25 mass % of alcohol) are used as automotive fuels. Alcohol additives reduce carbon dioxide liberation and thus improve the environmental performance of fuels. At present, alcohols are most often produced by fermentation of food raw materials containing hydrocarbons. Biosynthesis is environmentally and economically preferable, but the end fermentation products contain not only alcohols, but also various impurities including small amounts of water, which are usually removed by distillation, but this technology is costly, energy expensive and of limited use (in the case of, *e.g.*, azeotrope formation). Other drawbacks of the method are associated with the operating temperatures that cause the loss of microorganisms during biosynthesis. Therefore, pervaporation, which is conducted in milder conditions, becomes a popular energy- and resource-saving method of purification (mainly dehydration) of alcohols.[73–85]

Earlier, aqueous organic mixtures were separated using membranes made of natural polymeric materials and their derivatives.[1,2] A wide variety of polymeric and inorganic membranes have been tested; however, only a few of them meet the industrial requirements. Among the available range of polymeric materials, membranes based on polyheteroarylenes stand out because of high operating characteristics. The direction of selective mass transfer during pervaporation of aqueous organic mixtures is determined by the balance of hydrophilic–hydrophobic properties of the polymer membrane. In most cases, membranes based on

polyheteroarylenes exhibit dehydrating properties.[68, 70, 86–92]

Separation of water–ethanol mixture for, in particular, production of anhydrous alcohol for pharmaceutical industry and as major component of biofuels has attracted increased attention of researchers since the late 20th century. The transport properties of rigid-chain aromatic polyimides (BTDA-PDA, BTDA-BZD, PMDA-ODA, *etc.*, see Table 1) during pervaporation of water–ethanol mixture were studied.[91, 92] These polyimides have a dense structure and small free volume, which provides an explanation for high separation factor during pervaporation at low flux. Pervaporation of a water–ethanol mixture was studied at 323, 333, 338 and 343 K. It was found that the flux of the membranes increases with temperature; however, the correlation between the separation factor and temperature was not clear. It is believed[91, 92] that the changes in the transport properties with temperature are mainly related to the changes in the proportion of free volume in the membrane structure. For instance, raising the temperature increases the mobility of polymer chains in the membrane material; this favours an increase in the free volume and diffusion mobility of penetrants (both water and ethanol). As a consequence, the flux increases, but the separation factor may decline at the same time.

The dependence of the transport properties on the nature (*i.e.*, on the structure of the repeating unit) of polyheteroarylenes can be assessed by analyzing the properties of a number of polyimides containing different diamine moieties. The influence of the chemical structure of polyimides on the transport properties during pervaporation of aqueous ethanol solution containing up to 90 mass % of alcohol was studied.[93, 94] The introduction of bulky side substituents into the diamine group led to a looser packing of polymer chains and, as a consequence, higher permeability. For instance, the polyimide BHTDA-BADTB containing bulky side *tert*-butyl groups demonstrated a higher permeability than the other polyimides studied. The best combination of the flux and separation factor was found for the polyimide BHTDA-DBAPB which contains a more rigid and bulky diamine group. An increase in temperature from 298 to 328 K was accompanied by an increase in the flux and a decrease in the separation factor for all the membranes under investigation. This was explained[93, 94] by

Table 2. Transport properties of membranes based on polyheteroarylenes during dehydration of organic solvents methods by pervaporation.

Membrane material	Temperature /°C	Solvent	Solvent concentration (mass %)	Separation factor	Flux /g m^{-2} h^{-1}	Ref.
BTDA-PDA	45	Ethanol	88.9	1386	2.9	91
PMDA-DA (Kapton)	45	"	88.9	346	13.9	91
BTDA-BZD	60	"	88.9	2341	10.8	92
BHTDA-DBAPB	25	"	90.0	141	255	93
BHTDA-BADTB	60	"	90.0	15	325	94, 96
6FDA-NDA/DABA (9 : 1), (425 °C, 30 min)	25	"	85.0	119	133	95
6FDA-NDA/DABA (9 : 1), (cross-linked with ethylenediamine, 100 °C)	25	"	85.0	156	75.4	95
6FDA-NDA/DABA (9 : 1) [cross-linked with 1,4-bis(hydroxymethyl)benzene, 300 °C]	25	"	85.0	33	183	95
PVA (cross-linked with fumaric acid)	80	"	80.0	411	771	97
PVA (cross-linked with glutaraldehyde)	30	"	80.0	150	130	98
Chitosan-PVA (60 : 40)/PAN	50	"	50.0	2670	17.3	99
PAN-PEG-PAN	40	Acetone	95.0	17.5	130	100
PAN-PA	30	Ethanol	80.0	10.2	38	101
Ultem ®	60	Propan-2-ol	85.0	585	7	89
P84	60	"	85	16	2578	102
P84 (cross-linked with ethylenediamine)	60	"	85.0	604	534	102
PEI	50	"	88.0	270	1.1	103, 104
PEI/PANI-AA (5%)	50	"	88.0	400	6.5	103, 104
Matrimid	25	"	86.0	2000	1200	105
Matrimid/cyclodextrin (5%)	25	"	86.0	15000	1000	105
PBOZ	50	"	88.0	8990	3	106
PBO	80	"	90.0	670	135	107
PCA	50	"	88.0	8990	1.2	108
PCA/PPO	50	"	88.0	8990	14	108
PBO	80	n-Butanol	90.0	390	58	107
P84 (on ceramic support)	95	"	95.0	360	6000	109
P84	60	*tert*-Butyl alcohol	85.0	10 000	450	96
P84 (on ceramic support)	95	The same	95.0	150	4000	109
P84 (cross-linked in ethylenediamine vapours)	50	Acetone	85.0	53	1.8	110

Note. PVA is polyvinyl alcohol, PA is polyacrylic acid, PEG is poly(ethylene glycol), PAN is polyacrylonitrile and PPO is poly(phenylene oxide).

the enhanced mobility of polymer chains and by an increase in the proportion of free volume in the membrane material.

A new fluorine-containing copolyimide 6FDA-NDA/DABA (9 : 1) was tested as membrane material.[95] To prevent the membrane swelling, the polymer was modified using three different approaches, namely, thermal, diamino or diol cross-linking. All these modification techniques cause changes in the morphology and transport properties of the membrane during pervaporation dehydration of ethanol. Heat treatment at 425 °C is accompanied by decarboxylation-induced cross-linking, which restricts the membrane swelling and leads to an increase in the inter-chain distance in the polymer[95] and contributes to high fluxes and moderate separation factors of the membranes during pervaporation. Diamino cross-linking modification causes imide ring opening with the formation of amide bonds, but subsequent heating reverses the situation back. Diol cross-linking modification facilitates an increase in the inter-chain distance and restricts the membrane swelling, thus favouring higher fluxes at low separation factor values.

Table 2 summarizes data on pervaporation dehydration of organic solvents using membranes based on polyheteroarylenes and some other commercial polymers (these data are given for comparison).

Purification of propan-2-ol represents yet another field of application of pervaporation membranes. Pure propan-2-ol is a reactant for pharmaneutical industry, being also used as cleaning agent in, *e.g.*, semiconductor manufacturing and production of video display units. Commercial polyimides Ultem and P84 were tested as membrane materials for dehydration of alcohols, mainly propan-2-ol.[89, 96, 102, 111] It was found that heat treatment of the P84 polyimide membranes was followed by an increase in the inter-chain distances in the polymer and a decrease in the number of structural defects. Also, high-temperature treatment at 200 °C favours an increase in dehydration selectivity and a decrease in performance. On the contrary, low-temperature treatment at 100 °C significantly enhances the permeability but reduces the selectivity of the membrane. To improve the operating characteristics of P84 copolyimide during separation of water–propan-2-ol mixture, the membrane material was cross-linked with ethylenediamine; as a result, the membrane selectivity increased.[102] However, the cross-linking product demonstrated severe swelling during pervaporation owing to hydrophilic amide groups, thus reducing the overall selectivity of dehydration.

A classical method for modification of the properties of pervaporation membranes is to incorporate a modifier into the matrix of the membrane polymer. In particular, polyetherimide (PEI) was used as the polymer matrix while a copolymer of aniline (55 mass %) with anthranilic acid (45 mass %) (PANI-AA) was used as modifier.[103, 104] It was found that targeted modification of PEI with PANI-AA causes changes in the membrane morphology. PEI membranes containing 5 mass % of PANI-AA were tested in pervaporation of a water–propan-2-ol mixture containing up to 30 mass % of water, including the azeotropic mixture (12 mass % of water + 88 mass % alcohol). Owing to improved sorption and larger effective diffusion coefficients the modified membrane demonstrated a higher permeability and selectivity compared with the unmodified membrane during pervaporation of water–propan-2-ol mixture.

A cyclodextrin-modified Matrimid polyimide membrane for dehydration of propan-2-ol was studied.[105] The membrane exhibits high mechanical properties and stability against components of the liquid feed. Incorporation of small additives of a cyclodextrin derivative, namely, ethylenediamine-β-cyclodextrin, leads to formation of amide and hydrogen bonds with the polyimide backbone and thus makes the structure less permeable to bulky alcohol molecules. The introduction of cyclodextrin (up to 5 mass %) into the polyimide matrix leads to a decrease in permeability towards propan-2-ol and an increase in permeability to water, thus governing the increase in the separation factor. Introduction of larger amounts of the modifier (> 5 mass %) leads to loosening of the polyimide structure; this improves the flux of the membrane, but the separation factor declines simultaneously.

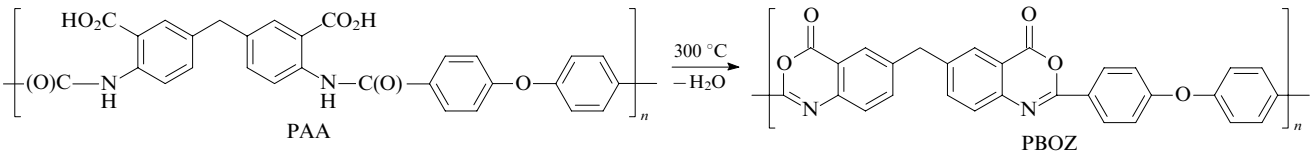
In the last decade, there has been a surge of interest in a particular group of heteroaromatic polymers, so-called thermally rearranged polyheteroarylenes. The specific structure of these polymers is due to nanoporosity emerging as a result of cyclization reaction and structural rearrangements in macromolecules under the action of high temperatures. Poly(benz[3,1]oxazin-4-one) (PBOZ), a novel polyheteroarylene obtained by thermal cyclization of its hydrolytically stable precursor, poly(amic acid) (PAA, Scheme 1), was studied.[106]

Heat treatment of the prepolymer, PAA, to give PBOZ causes not only densification of the polymer structure, but also the formation of an excess free volume (~4%) as a result of structural transformations in the membrane; this improves the main transport parameters of gas separation and pervaporation processes.

Scanning electron microscopy (SEM) images of cross-sections of a PBOZ membrane (Fig. 2) clearly demonstrate blind pores 30–60 nm in diameter. The pores, which determine the excess free volume, were formed upon removal of water and thermal cyclization. The transport and selective properties of this PBOZ membrane were studied taking pervaporation of a water–propan-2-ol mixture as an example. The membrane appeared to be inert towards the alcohol, while the excess free volume facilitated transport of water molecules through the PBOZ matrix. Experiments revealed high selectivity and a moderate permeation flux of the PBOZ membrane during dehydration of propan-2-ol.

Yet another representative of thermally rearranged polyheteroarylenes is acetate-containing polyimide polybenzoxazole (PBO), which seems to a promising membrane material for dehydration of aqueous alcohol mixtures in production of biofuels.[107] PBO membranes exhibit high

Scheme 1



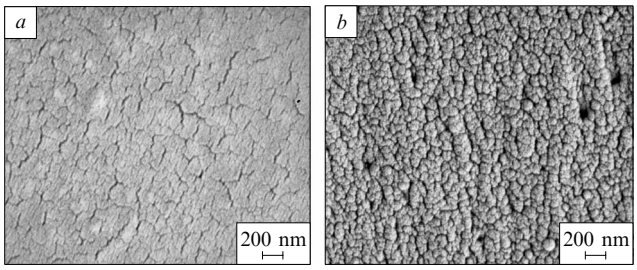


Figure 2. SEM images of PAA (*a*) and PBOZ (*b*) membranes.[108]

chemical and thermal stability and are characterized by high flux and separation factor, as was revealed by the experiments on pervaporation of ethanol–water, n-butanol–water and propan-2-ol–water mixtures. Clearly, the results obtained offer great prospects for industrial applications of PBO membranes.

When studying membrane materials based on polyheteroarylenes, one should take into account the fact that they can contain residual solvent after completion of all steps of the synthesis procedure. The presence of residual solvent is due to complexation between polyheteroarylenes and aprotic solvents in the forming solutions. The effect of residual solvent was studied[108] in the experiments on pervaporation of water–propan-2-ol mixture using a membrane made of a novel polyheteroarylene, namely, polycarbamide (PCA) bearing an amide group incorporated into the backbone. Two types of membranes investigated were a PCA(MP) membrane prepared by casting and containing residual solvent (*N*-methylpyrrolidone, MP) and a solvent-free PCA membrane prepared by immersion of the PCA(MP) membrane into methanol for 3 days followed by drying at 50 °C *in vacuo* until constant mass. The amount of the residual solvent on the PCA(MP) membranes was ~14.6 mass %.

Figure 3 presents the plots of the separation factor and membrane permeability *vs.* water content in the feed. For both types of membranes, the permeate is substantially enriched with water. The membranes exhibit high selectivity during separation of water–propan-2-ol mixtures in a wide range of compositions.

The permeability of the PCA(MP) membrane is much higher than that of the PCA membrane. Probably, the residual amide solvent acts as a plasticizer facilitating swelling and diffusion of molecules of the liquids being separated. This example shows that the transport and sorption parameters of polymeric membranes depend on both the chemical nature and structure of monomer unit and on the ability of functional groups to participate in specific interactions with penetrant and solvent. Here, complexation through hydrogen bonding or dipole–dipole interactions leads to changes in the physicochemical properties of the polymers and eventually to changes in the transport parameters. Also, complexation with the solvent in some cases causes the formation of supramolecular structure of polyheteroarylenes.

Often, homogeneous membranes based on polyheteroarylenes exhibit high selectivity but relatively low performance. To improve this parameter, a composite membrane with a thin selective PCA layer on porous poly(phenylene oxide) (PPO) support was prepared. The photomicrograph

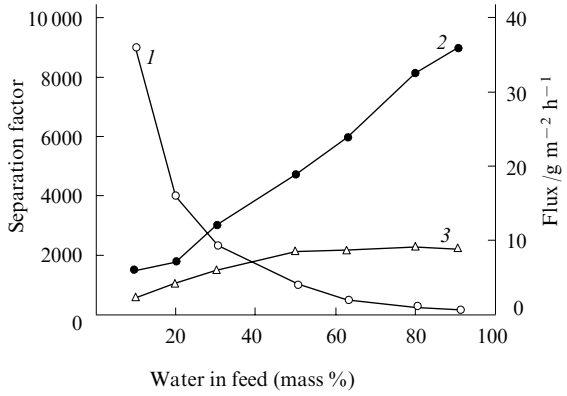


Figure 3. Separation factor (*1*) and flux (*2*, *3*) plotted *vs.* water concentration in the water–propan-2-ol feed in pervaporation using PCA(MP) (*1*, *2*) and PCA (*1*, *3*) membranes.[108]

of cleaved cross-section of the homogeneous PCA membrane (Fig 4 *a*) shows that the membrane has a dense, relatively homogeneous structure. The photomicrograph of cleaved cross-section of the composite membrane (see Fig. 4 *b*) demonstrates the structure of the dense PCA surface layer (6 μm thick) and a fragment of the layer of porous PPO support with sponge-like structure.

The transport properties of a PCA/PPO composite membrane were studied during pervaporation of water–propan-2-ol mixtures in a wide range of concentrations.[108] The dependence of the separation factor on the water content in the feed (Fig. 5) demonstrates that high selectivity of the homogeneous PCA membrane also holds for the PCA/PPO composite membrane. The dependence of the flux on the composition (see Fig. 5 *b*) indicates a substantially higher (by a factor of nearly 12) permeability of the composite membrane compared to the permeability of the homogeneous membrane.

Composite membranes with thin selective layers of industrial polyimides Matrimid, Torlon and P84 on ceramic supports were studied during separation of water–n-butanol mixtures.[109] The highest efficiency was achieved for the composite membrane with the P84 polyimide selective layer. The membrane lifetime was as long as 140 days at temper-

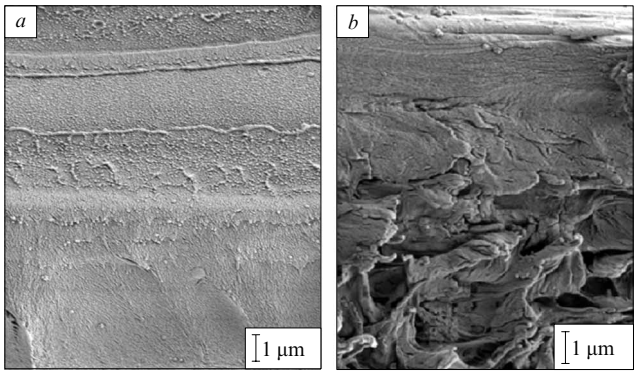


Figure 4. SEM imags of cross-sections of a homogeneous PCA membrane (*a*) and composite PCA/PPO membrane (*b*).[108]

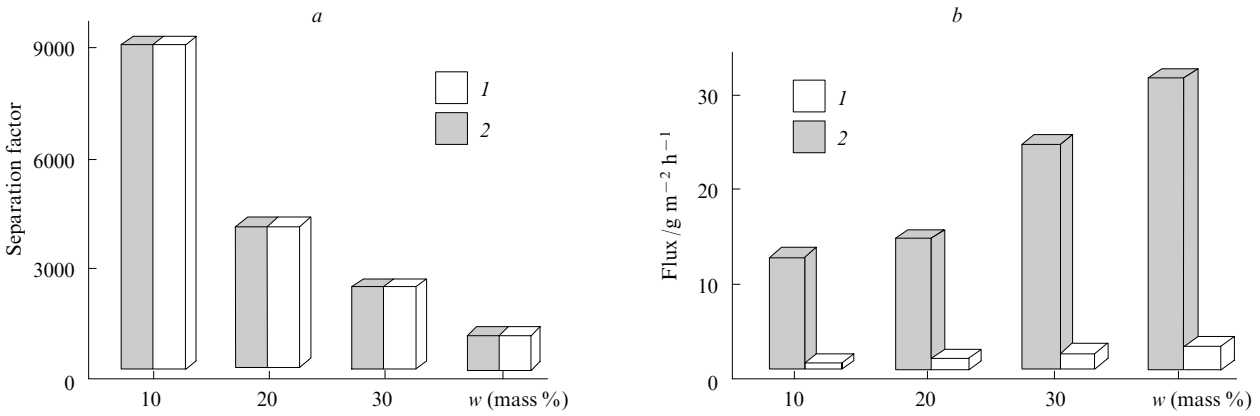


Figure 5. Separation factor (*a*) and flux (*b*) plotted *vs.* water content (*w*) in water–propan-2-ol feed mixture during pervaporation using PCA membranes (*1*) and PCA/PPO composite membranes (*2*).[108]

atures to 150 °C. The composite membrane with the P84 selective layer was also used for separation of a water–*tert*-butyl alcohol mixture. The membrane exhibited high operating characteristics; the penetrant was mainly *tert*-butyl alcohol. The lifetime of this membrane in the experiments on separation of aqueous organic mixtures was much longer (up to 250 days). These parameters, including the operating stability of separation properties, make the membranes promising for industrial applications.

Compared with considerable literature on pervaporation of water–alcohol mixtures using membranes based on polyheteroarylenes, there are few publications devoted to dehydration of other organic compounds. In particular, dehydration of acetone using P84 copolyimide pervaporation membranes cross-linked in ethylenediamine vapour was studied.[110] It was found that the cross-linking temperature influences the transport properties of the membranes, *viz.*, the higher the temperature of ethylenediamine vapour the higher the cross-link density and the separation factor and the lower the flux. The cross-linking time and the separation factor are related nonlinearly. The best results for dehydration of acetone–water (85 : 15 by mass) mixture at 50 °C are as follows: the separation factor is 53 and the flux is 1.8 kg m^{-2} h^{-1}.

V. Removal of organics from water

Practical orientation of research activity aimed at developing membrane methods for removal of organics from water is to a great extent due to problems in environmental protection. In particular, removal of hazardous organics (trichloroethylene, chloroform, dichloromethane, benzene, toluene, phenol, *etc.*) from industrial wastewater is of high environmental value. Also, removal of organic impurities from aqueous solutions by membrane methods is a challenge because preferred transport of organic species is not always achieved even using organophilic membranes. In the case of pervaporation, the permeability selectivity is often lower than the sorption selectivity and thus pervaporation has no explicit advantages over sorption in removal of organics from water.[4] However, if the concentration of organics in water is relatively high, many advantages of pervaporation manifest themselves. These are first of all continuous character of the process and the absence of such sorption drawbacks as limitations due to sorption saturation.

Various organophilic membranes with enhanced selectivity towards organic solvents have been designed to remove organics from water. Examples are provided by membranes based on polyurethanes, poly(dimethylsiloxane) and poly(dimethylsilylpropyne); they are efficient in separation of organic components from aqueous organic mixtures.[112–121] Fluorine- and silicon-containing polyheteroarylenes characterized by sufficiently high separation factors in the case of aqueous organic media are also available. Polyimides 6FDA-PFDAB with fluorine-containing groups in the dianhydride and diamine groups were studied as membrane material for purification of wastewater from organics.[90] Fluoroalkyl substituents in polyimides enhance their hydrophobicity and increase the proportion of free volume in the membrane structure. This improves the efficiency of pervaporation separation using fluorinated polyimides compared with the unmodified analogues. It was found that an increase in the concentration of the organic component in the feed as well as raising the temperature cause the specific flux to increase and the separation factor to decrease. As the residual pressure under the membrane increases, another trend is observed, *viz.*, the separation factor increases but the flux declines. This was explained[90] by the influence of structural features of the membranes and by the effect of the free volume which increases with temperature.

Polysiloxaneimide is a promising material for separation of organics. The transport properties of 6FDA-SIDA polysiloxaneimide membranes were studied in the experiments on separation of volatile organic compounds (dichloromethane, trichloroethylene, toluene) from water by pervaporation.[122] It was shown that all polysiloxaneimide membranes have high pervaporation selectivity and flux towards hydrophobic organic compounds. The highest selectivity and flux were obtained in separation of toluene from its mixtures with water.

Novel membranes made of fluorine-containing polysiloxane–imide copolymers FD5000 [89% or 94% poly(dimethylsiloxane) (PDMS)] for removal of ethanol and phenol from aqueous solutions have been designed.[123] It was found that an increase in the number of siloxane units improves the membrane hydrophobicity and the permeabil-

ity of ethanol and phenol. Fluorine-containing groups in the polyimide units as well as high concentration of siloxane units favour enhanced sorption of ethanol by the membranes compared with the poly(dimethylsiloxane) membranes. Fluorine-containing polysiloxane–imide copolymers exhibit optimum transport properties for pervaporation of aqueous ethanol and phenol solutions.

Another type of membranes made of fluorine-containing polysiloxane–imide copolymers (6FDA/SIDA50-PFDAB50) was prepared by polycondensation using siloxane diamine and fluorinated diamine and tested in pervaporation of organic components, in particular, trichloroethylene, from water.[124] High content of siloxane units in the copolyimide membranes ensures low density and large part of free volume compared to the copolyimides with high content of fluorinated units. The polyimides with siloxane units are characterized by two glass transition temperatures, thus being microheterophase separated structures. An increase in the siloxane-to-fluorinated unit ratio improves the sorption and diffusion properties towards organic compounds and, hence, leads to considerable increase in the flux and separation factor. The copolyimides containing equal amounts of the siloxane and fluorinated units [50 : 50 (mol.%)] exhibited an optimum flux and separation factor, in particular, in the separation of trichloroethylene from aqueous solutions.

A study of organophilic pervaporation using fluorinated siloxane–imide block copolymers PSI-3 revealed similar correlations between the structure and transport properties.[125] Also, it was shown that the introduction of siloxane units improves the transport properties of membranes but their mechanical strength decreases.

To improve the mechanical strength, a composite membrane comprising a thin PSI selective layer, porous polyetherimide and a non-woven fabric as support was developed.[126] Experiments on separation of organics from water carried out at different temperatures using aqueous ethanol, propan-2-ol and acetone solutions as examples revealed efficient operation of the composite membrane and showed that raising the temperature leads to an increase in both the flux and the separation factor.

The transport properties of membranes based on polyheteroarylenes and a number of commercial polymers (data are shown for comparison, see Refs 117, 127 and 128) in separation of organics from water are listed in Table 3.

VI. Separation of organic liquid mixtures

Researchers pay considerable attention to separation of organic liquid mixtures because of industrial demands for efficient methods of separation of, *e.g.*, benzene–cyclohexane, benzene–hexane, toluene–heptane, ethylbenzene–xylene, *p*-xylene–*o*-xylene mixtures, *etc*. Components of these mixtures have similar physicochemical properties and are hard to separate by conventional methods. At present, there has been continuous search for novel membrane materials that should exhibit not only selectivity, but also chemical stability against the organic components being separated.[73, 129–133]

According to the solution–diffusion mechanism, efficient pervaporation separation of organic liquids can be conducted using the mobility difference between the components permeating the membrane material. To this end, appropriate membrane materials include rigid-chain glassy polymers because they are more selective towards the shape and size of molecules of the liquids being separated. In addition, one should provide for the possibility of cross-linking of the glassy polymers to suppress the plasticization effect of penetrants in order to maintain or even to improve the diffusion selectivity. As an example, a toluene–isooctane mixture was separated using membranes prepared from rigid-chain glassy copolymers of polyimides containing cross-linkable fragments of 3,5-diaminobenzoic acid.[134] Incorporation of these units into the polyimide structure results in denser packing of macromolecules, a decrease in the free volume in the membrane and restricts the membrane swelling in the liquids being separated. A good correlation between the diffusion selectivity and the proportion of free volume in the 'cross-linked' membranes was revealed. Also, by specifying a constant free volume in the membranes the diffusion selectivity can be increased from 1 to 18. There exists a synergistic effect of sorption and diffusion on the membrane permeability and sorption

Table 3. Transport properties of membranes in removal of organics from aqueous organic solutions.

Membrane material	Temperature /°C	Organic compound [concentration (mass %)]	Separation factor	Flux /kg m^{-2} h^{-1}	Ref.
6FDA-PFDAB	30	Dichloromethane (1.0)	160	0.03	90
6FDA-PFDAB	30	Trifluoroethylene (0.11)	400	0.015	90
6FDA-SIDA	30	Dichloromethane (0.05)	2250	0.24	122
6FDA-SIDA	30	Trichloroethylene (0.05)	5000	0.38	122
6FDA-SIDA	30	Toluene (0.05)	9000	0.46	122
FD5000 (94% PDMS)	60	Ethanol (10.0)	10.6	0.56	90
FD5000 (89% PDMS)	60	Phenol (5.0)	22	2.4	123
FDA/SIDA50-PFDAB50	25	Trichloroethylene (0.05)	2170	0.025	124
PSI-3	25	Trichloroethylene (0.05)	3270	27.6	125
PSI/PEI (composite membrane)	60	Ethanol (5.0)	3	500	126
PDMS/PVDF	30	n-Butanol (1.0)	43	159.6	127
PPhS/PDMS/PVDF	30	n-Butanol (1.0)	46.8	261.4	127
PDMS	55	n-Butanol (1.5)	41.7	704.6	128
PDMS/PAN	42	n-Butanol (3.5)	22	1.67	117

Note. PVDF is poly(vinylidene fluoride) and PPhS is polyphenylsiloxane.

selectivity, which increased from 3.5 to 5.0 upon cross-linking. The overall separation factor increased to a value of 90.

The possibility of pervaporation separation of mixtures of aromatic and nonaromatic hydrocarbons (benzene–cyclohexane, benzene–n-hexane) using several series of polyimide membranes was studied.[135,136] The BPDA-TMPD membranes were modified by introducing phosphonate ester groups and cross-linked thermally and then with diamine.[135] A phosphorylation degree of the polyimide of up to 200% (two phosphonate ester groups per repeating unit) was achieved. The membranes were tested in pervaporation and sorption experiments using benzene–cyclohexane and benzene–n-hexane mixtures. The pervaporation performance was dependent on the phosphorylation degree and on the degree of cross-linking. It was established that the phosphorylated and cross-linked membranes are characterized by higher flux compared to the initial uncross-linked polyimide membrane. High pervaporation selectivity was related to high sorption selectivity owing to the affinity of phosphonate ester groups to benzene.

Another series of copolyimides containing diethynylbenzidine moiety was also investigated.[136] A pervaporation study of a benzene–cyclohexane mixture showed that cross-linking of these copolyimides causes the separation factor to increase and the flux to decrease as compared to those of the uncross-linked analogues. Sorption studies revealed that the increase in the separation factor of the cross-linked membranes is mainly determined by the increase in the diffusion selectivity. In addition, tetracyanoethylene (TCNE), an electron acceptor having a high affinity to ethynyl-containing and aromatic compounds, was homogeneously dispersed in one of the polyimide matrices. The membrane thus prepared demonstrated high performance during pervaporation of benzene–cyclohexane and toluene–isooctane mixtures. The addition of TCNE to uncross-linked copolyimides also favoured an increase in the separation factor due to not only enhanced diffusion selectivity, but also improved sorption selectivity.

Membranes based on aromatic (ethylene oxide imide) copolymer (PEO-PI) were studied taking benzene–n-hexane and benzene–cyclohexane mixtures as examples.[137] The results of pervaporation experiments were interpreted taking into account the sorption and diffusion properties of the membranes. It was found that the sorption and desorption behaviour of pure vapours obey the Fick law, whereas the corresponding dependences for binary mixtures show some deviations. The separation factor was higher for the benzene–cyclohexane mixture, which was explained by the sorption and diffusion selectivity during pervaporation.

The same authors also studied the sorption and transport properties during the separation of benzene–n-hexane and benzene–cyclohexane mixtures using sulfonyl-containing DSDA-DDBT polyimide membranes.[138] It was shown that the sorption isotherms of individual components and binary mixtures do not obey the Fick law. Lower sorption selectivity in the experiments with the benzene–cyclohexane mixture compared to the benzene–n-hexane system can be due to the close parameters of the of interaction of cyclohexane and benzene with the membrane polymer. The averaged diffusion coefficients were calculated from the sorption and pervaporation data. The influence of the competitive components of the feed on the diffusion coefficients was revealed. For instance, the diffusion coefficient of the penetrant with smaller molecules decreased in the presence of the penetrant having larger molecules, and *vice versa*. The lowest diffusion coefficient was found for cyclohexane molecules. The membranes in question were characterized by good flux and rather high selectivity during the separation of mixtures of aromatic and nonaromatic hydrocarbons. It was pointed out that if such mixtures are separated using membranes prepared from copolyimides containing rigid and flexible segments, the latter exhibit preferred affinity to the aromatic component of the mixture and provide selective permeability of the membrane, whereas rigid segments are responsible for the mechanical strength of the membrane.

An attempt to separate a mixture of *o*-xylene and *p*-xylene using cross-linked fluorine-containing copolyimide membranes was reported.[139] Fluorine-containing copolyimides contained cross-linkable fragments of 3,5-diaminobenzoic acid, which made it possible to use ethylene glycol and hexamethylenediamine as cross-linking agents to form the diester bond and for diamide cross-linking, respectively. All membranes exhibited high chemical and thermal stability during the separation of the *o*-xylene–*p*-xylene (50 : 50) feed at 60 °C. The flux of the membranes was dependent on the structure of the monomer unit and on the cross-linking agent chosen. The transport parameters were not high, *viz*., the specific flux was 0.04–25.0 kg μm m^{-2} h^{-1} and the separation factor was 1.15–1.47.

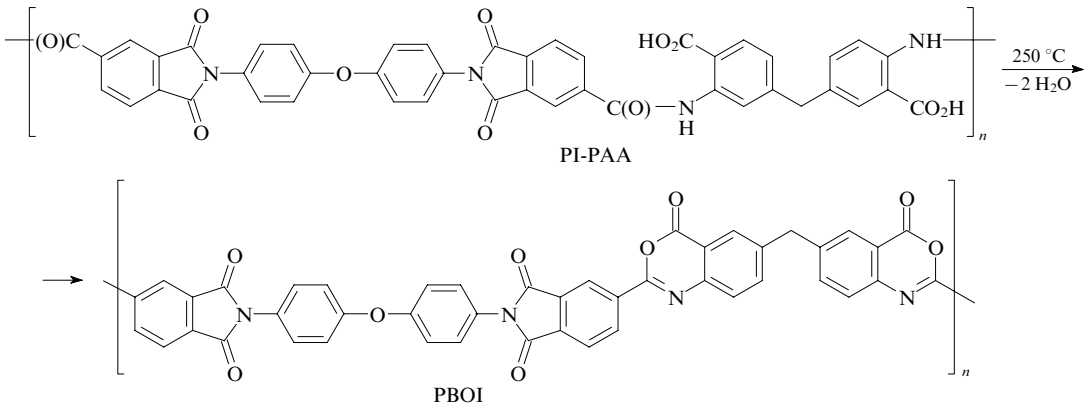
Pervaporation of n-heptane–thiophene mixture in the temperature range from 40 to 77 °C was studied[140] in connection with solution to the problem of removal of sulfur-containing compounds from light oil. Soluble fluorine-containing polyimides 6FDA-MDA were synthesized and asymmetric membranes were prepared by phase inversion. The efficiency of separation was characterized by the specific flux ranging from 0.56 to 1.68 kg μm m^{-2} h^{-1} and the sulfur enrichment factor of permeate lying between 2.24 and 3.12.

To separate mixtures of aromatic and aliphatic hydrocarbons by pervaporation, a series of aromatic copolyimides containing ether or siloxane units was synthesized.[141] Pervaporation of toluene–n-heptane and benzene–n-heptane mixtures was conducted at 60 and 80 °C, respectively. All polymers were selective towards the aromatic hydrocarbon. The introduction of siloxane units into the polymer led to an increase in the fluxes, but the selectivity of separation of the hydrocarbons declined. Incorporation of ether groups caused neither large increase in permeability nor large decrease in separation factor.

Separation of mixtures of polar and nonpolar liquids, namely, methanol and cyclohexane, is topical owing, in particular, to the formation of an azeotropic mixture containing 37.2 mass % of methanol and 62.8 mass % of cyclohexane at 20 °C, 760 mm Hg.[142] Imide-containing poly(amic acid) (PI-PAA) was studied;[143] the compound is a prepolymer of polybenzoxazinoneimide (PBOI) (Scheme 2).[144]

PI-PAA exhibits high physicomechanical properties, high thermal stability and hydrolytic stability, which makes it attractive membrane material for pervaporation. The transport properties were studied using a bilayer composite membrane comprising a thin layer of PI-PAA and a porous asymmetric poly(phenylene oxide) support.[145] Figure 6 presents the selectivity of separation of methanol–cyclohexane (CyH) mixture and the permeate flux plotted

Scheme 2



vs. methanol concentration in the feed. The highest separation factor $\alpha_{MeOH/CyH} \geqslant 1000$ was achieved during the pervaporation of a mixture with low content of methanol (10 mass %).

Separation of a methanol–cyclohexane mixture was studied using membrane based on a composite obtained by incorporating polyaniline (PANI, 3 mass %) into the polyetherimide (PEI) matrix.[145] It was found that PANI additives improve the flux of the membrane and have almost no effect on the separation factor during pervaporation of a mixture containing 10 mass % of methanol. The separation selectivity of this mixture is very high (2300) because cyclohexane is inert towards PEI.

The same type of composite membrane, PEI/PANI, was tested taking the separation of the methanol–toluene mixture characterized by an azeotropic point [methanol : toluene = 69 : 31 (mass %) at 20 °C and 760 mm Hg].[104, 145, 146]

From the data in Fig. 7 is follows that the introduction of PANI (6 mass %) leads to an increase in the separation factor and to a slight decrease in the flux through the membrane. The reason is that PANI facilitates a decline in the sorption capacity of the membranes towards the components of the feed mixture and an increase in the polymer–solvent interaction parameter.

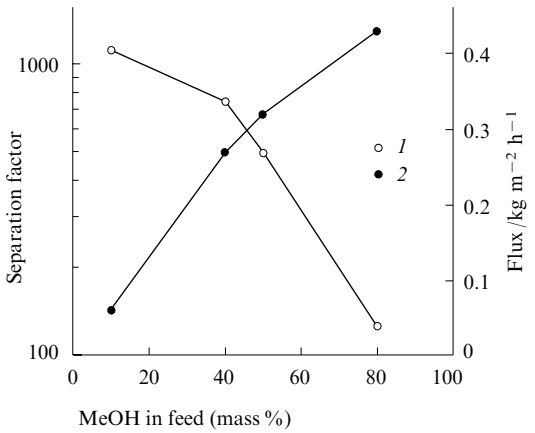


Figure 6. Separation factor (*1*) and flux (*2*) plotted *vs*. methanol concentration in feed in pervaporation of the methanol–cyclohexane mixture using PI-PAA/PPO membranes at 50 °C.[143]

Particular attention was paid[146] to the separation of methanol–toluene azeotropic mixture (Fig 8). As the PANI content increased, the separation factor of the azeotropic mixture also increased, but the flux through the membrane decreased in accordance with the 'slope opposition' rule for these parameters. The results of pervaporation experiments are consistent with the sorption-diffusion properties of this system. A decrease in the flux with increasing PANI content is due to a decrease in the free volume. An increase in selectivity is a consequence of an increase in the methanol

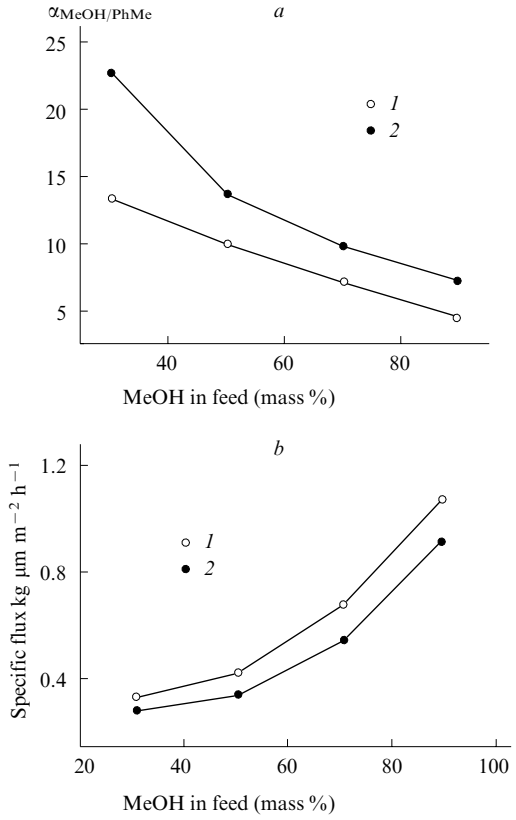


Figure 7. Separation factor (*a*) and specific flux (*b*) plotted *vs*. methanol concentration in feed in pervaporation of the methanol–toluene mixture using different membranes at 50 °C.[145] Membrane: PEI (*1*) and PEI/6% PANI (*1*).

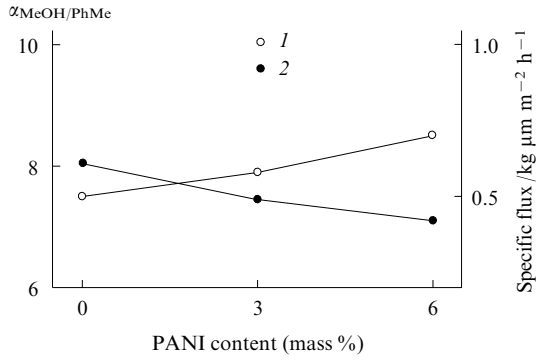


Figure 8. Separation factor (*1*) and specific flux (*2*) of PEI/PANI membranes plotted *vs.* PANI content (in mass %) in pervaporation of methanol–toluene azeotropic mixture (69 : 31 by mass) at 50 °C.[104, 146]

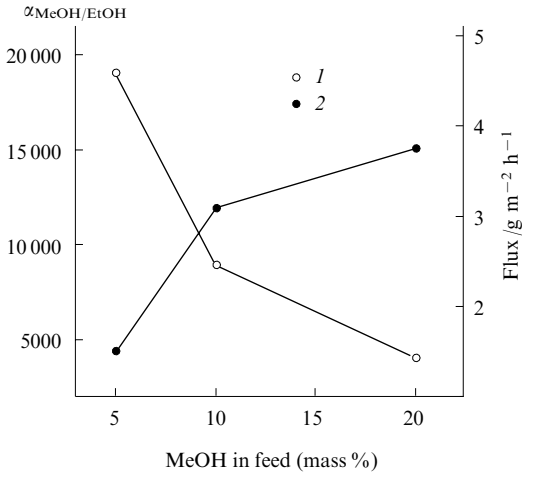


Figure 9. Separation factor (*1*) and flux (*2*) of PBOI membrane plotted *vs.* methanol concentration in feed in pervaporation of the methanol–ethanol mixture at 20 °C.[144]

diffusion rate and a considerable increase in the difference between the diffusion coefficients of methanol and toluene.

Purification of ethanol from methanol is a technically sophisticated problem. Published data on separation of this mixture are scarce. Microporous ceramic membranes used for pervaporation of a mixture of ethanol with 5 mass % of methanol and characterized by a separation factor of 17 and 9.8 at a flux of 0.27 and 0.8 kg m^{-2} h^{-1}, respectively, were studied.[147, 148] A polymeric membrane for separation of a methanol–ethanol mixture was proposed for the first time recently.[144] The membrane material, PBOI, is a polyheteroarylene containing imide and oxazinone fragments in the backbone. Owing to this structure at molecular masses from 50 000 to 100 000 Da, PBOI exhibits good physicomechanical properties and is thermally stable up to 400 °C; also, it is insoluble in many conventional solvents. Note also that PBOI membranes were not used earlier for pervaporation. The PBOI pervaporation membrane[144] enables targeted separation of methanol–ethanol mixtures with high selectivity (to 19 000) (Fig. 9) and, in particular, remove methanol from ethanol solutions obtained in the course of fermentation.

Table 4. Transport properties membranes based on polyheteroarylenes in pervaporation separation of organic mixtures.

Membrane material[a]	Temperature /°C	Feed [component ratio (mass %)]	Separation factor	Specific flux /g μm m^{-2} h^{-1}	Ref.
6FDA-DAM/DABA	100	Toluene–isooctane (80 : 20)	90	1	134
BPDA-TMPD (phosphorylated) 10 (171%)	70	Benzene–cyclohexane (20 : 80)	32	2500	135
BPDA-TMPD (phosphorylated) 7 (155%)	70	Benzene–n-hexane (60 : 40)	8.8	4600	135
DSDA-TrMPD/DEB (3 : 1) (TCNE 10%)	70	Benzene–cyclohexane (50 : 50)	48	440	136
DSDA-TrMPD/DEB (3 : 1) (TCNE 10%)	70	Toluene–isooctane (45 : 55)	330	1100	136
PEO-PI-1	60	Benzene–n-hexane (40 : 60)	7.5	28	137
PEO-PI-1	60	Benzene–cyclohexane (60 : 40)	4.7	70	137
DSDA-DDBT	60	Benzene–n-hexane (17 : 83)	10.6	1033	138
DSDA-DDBT	60	Benzene–cyclohexane (8 : 92)	102	77	138
6FDA-6FpDA/4MPD/DABA	60	*p*-Xylene–*o*-xylene (50 : 50)	1.25	24	139
6FDA-MDA	77	n-Heptane–thiophene (1 : 99)	1.68	3.12	140
FDA-BTDA	80	Toluene–n-heptane (40 : 60)	7.0	1.34	141
4MPD/ATPEPG (30 : 70)-BTDA	80	Benzene–n-heptane (40 : 60)	5.4	10.68	141
FDA/ATDS (50 : 50)-DSDA	60	Toluene–n-heptane (19.5 : 80.5)	2.2	11.15	141
PI-PAA/PPO (composite membrane)	50	Methanol–cyclohexane (10 : 90)	1100	400	143
PEI	50	Methanol–cyclohexane (10 : 90)	2300	1150	145
PEI/PANI (3%)	50	Methanol–cyclohexane (10 : 90)	2300	1840	145
PEI	50	Methanol–toluene (69 : 31)	8	600	103, 146
PEI/PANI (3%)	50	Methanol–toluene (69 : 31)	6	800	103, 146
PBOI	20	Methanol–ethanol (5 : 95)	19 000	36	144
PU	25	Benzene–cyclohexane (54 : 46)	325	2.7	149
PHPVAC	25	Benzene–cyclohexane (50 : 50)	500	7.5	150
PEO 400	80	Toluene–n-heptane (20 : 80)	690	7.3	151

[a] The designations were taken from original publications. PHPVAC is partially hydrolyzed poly(vinyl acetate) and PU is polyurethane.

Table 4 summarizes the data on the separation of organic mixtures using membranes based on polyheteroarylenes and a number of commercial polymers (data are given for comparison, Refs 149–151).

VII. Conclusion

Our analysis of published data substantiates the promise of utilization of polymer films based on polyheteroarylenes as membrane materials for pervaporation. This is first of all due to their physicochemical properties (often, unique ones), in particular, high structural ordering and fixed free volume. In addition, materials presented in the review suggest that structural rearrangements in the polymers as well as variation of experimental conditions lead to significant changes in the separation properties of the membranes. At the same time, it should be noted that to date, information on the dependence of the transport properties of membranes based on polyheteroarylenes on both external and intrinsic factors is scarce. Nevertheless, the results presented above confirm that the title membrane materials are promising for separation technology compared with other types of membranes, *e.g.*, microporous ceramic ones. This conclusion is well illustrated by the examples of separation of some industrially important mixtures, *e.g.*, methanol–ethanol, benzene–cyclohexane, *etc*. Attempts to separate mixtures of xylene isomers, aromatic, aliphatic and alicyclic compounds have been reported. Prospects for practical application of these advanced materials in diffusion separation of liquids are associated with not only the expected high efficiency, but also adaptation to various external conditions owing to such physicochemical properties as the chemical stability, high strength, thermal stability, *etc*. By and large, analysis of the results of studies on the diffusion membranes based on polyheteroarylenes allows one to expect further advances in this research field.

The authors express their gratitude to Dr. T K Meleshko, Senior Researcher at the Institute of Macromolecular Compounds, Russian Academy of Sciences, for valuable comments in the course of preparation of the manuscript. They also acknowledge Saint Petersburg State University for financial support within the framework of a research grant (Project No. 12.38.257.2014).

A Yu Pulyalina is grateful to the Scholarship of the President of the Russian Federation for financial support (Project No. 184, SP-1469.2015.1).

References

1. *Membrany i Membrannye Tekhnologii* (Membranes and Membrane Technologies) (Ed. A B Yaroslavtsev) (Moscow: Nauchnyi Mir, 2013)
2. R W Baker *Membrane Technology and Applications* (3rd Ed.) (Wiley, 2012)
3. R Singh *Membrane Technology and Engineering for Water Purification* (2nd Ed.) (Elsevier, 2015)
4. S Álvarez, F A Riera, R Álvarez, J Coca, F P Cuperus, S Th Bouwer, G Boswinkel, R W van Gemert, J W Veldsink, L Giorno, L Donato, S Todisco, E Drioli, J Olsson, G Trägårdh, S N Gaeta, L Panyor *J. Food Eng.* **46** 109 (2000)
5. A A Babalou, N Rafia, K Ghasemzadeh, in *Pervaporation, Vapour Permeation and Membrane Distillation (Woodhead Publ. Ser. in Energy* Vol. 77) (Eds A Basile, A Figoli, M Khayet) [Woodhead Publ. (Elsevier), 2015] p. 65
6. G Genduso, P Luis, B Van der Bruggen, in *Membrane Reactors for Energy Applications and Basic Chemical Production. (Woodhead Publ. Ser. in Energy* Vol. 76) (Eds A Basile, A Figoli, M Khayet) [Woodhead Publ. (Elsevier), 2015] p. 565
7. N L Basov, M M Ermilova, N V Orekhova, A B Yaroslavtsev *Russ. Chem. Rev.* **82** 352 (2013)
8. V V Volkov, E G Novitskii, G A Dibrov, P V Samokhin, M A Kipnis, A B Yaroslavtsev *Catal. Today* **193** 31 (2012)
9. V M Vorotyntsev, P N Drozdov, E Y Kolotilov *Desalination* **149** 23 (2002)
10. Terminologiya (Terminology) *Membr. Membr. Tekhnol.* **3** 74 (2013)
11. G F Voronin *Osnovy Termodinamiki* (Fundamentals of Thermodynamics) (Moscow: Moscow State University) 1987
12. M Mulder *Basic Principles of Membrane Technology* (Heidelberg: Kluwer Academic, 1996)
13. P D Chapman, T Oliveira, A G Livingston, K Li *J. Membr. Sci.* **318** 5 (2008)
14. L Y Jiang, Y Wang, T -S Chung, X Y Qiao, J-Y Lai *Prog. Polym. Sci.* **34** 1135 (2009)
15. P A Kober *J. Am. Chem. Soc.* **39** 944 (1917)
16. A H Ballweg, H E A Brüschke, W H Schneider, G F Tüsel, K W Böddeker, in *Proceedings of Fifth International Alcohol Fuel Technology Symposium, Auckland, 1982* p. 97
17. H E A Brüschke, N P Wynn, in *Encyclopedia of Separation Science* (Eds M Cooke, C F Poole) (Elsevier, 2000) p. 1777
18. R W Baker, in *Encyclopedia of Separation Science* (Eds M Cooke, C F Poole) (Elsevier, 2000) p. 189
19. S P Chopade, S M Mahajani, in *Encyclopedia of Separation Science* (Eds M Cooke, C F Poole) (Elsevier, 2000) p. 3636
20. S I Semenova *Krit. Tekhnologii. Membrany* (9) 3 (2001)
21. Yu E Kirsh, Yu A Fedotov, S I Semenova, P A Vdovin, V V Valuev, O Yu Zemlianova, S F Timashev *J. Membr. Sci.* **103** 95 (1995)
22. A Jonquières, R Clément, P Lochon, J Néel, M Dresch, B Chrétien *J. Membr. Sci.* **206** 87 (2002)
23. E P Ageev, N N Matushkina, N L Strusovskaya *Membr. Membr. Tekhnol.* **3** 231 (2013)
24. V V Volkov *Russ. Chem. Bull., Eng. Ed.* **43** 187 (1994) [*Izv. Akad. Nauk, Ser. Khim.* 208 (1994)]
25. A V Storonkin *Termodinamika Geterogennykh Sistem* (Thermodynamics of Heterogeneous Systems) (Leningrad: Leningrad State University, 1967) Pts 1, 2
26. L A Serafimov *Theor. Found. Chem. Eng.* **35** 237 (2001) [*Teoret. Osnovy Khim. tekhnol.* **35** 252 (2001)]
27. P K Ten, R W Field *Chem. Eng. Sci.* **55** 1425 (2000)
28. S C George, S Thomas *Prog. Polym. Sci.* **26** 985 (2001)
29. J Huang, Y-C Wang, C-L Li, K-R Lee, S-C Fan, T-T Wu, J-Y Lai *Eur. Polym. J.* **38** 179 (2002)
30. P Uchytil, R Petričkovič *J. Membr. Sci.* **209** 67 (2002)
31. S R de Groot, P Mazur *Non-Equilibrium Thermodynamics* (Amsterdam: North-Holland Publ., 1962)
32. E P Ageev *Krit. Tekhnologii. Membrany* (9) 42 (2001)
33. Y Demirel *Nonequilibrium Thermodynamics: Transport and Rate Processes in Physical and Biological Systems* (Amsterdam: Elsevier, 2002)
34. D Kondepudi, I Prigogine *Modern Thermodynamics: From Heat Engines to Dissipative Structures* (New York: Wiley, 1998)
35. O Kedem *J. Membr. Sci.* **47** 277 (1989)
36. A M Toikka, A V Penkova, D A Markelov *Int. J. Heat Mass Transfer* **72** 423 (2014)
37. A A Ghoreyshi, F A Farhadpour, M Soltanieh, M Abdelghani *J. Membr. Sci.* **211** 215 (2003)
38. Y Fang, L Bian, X Wang *J. Memb. Sci.* **437** 72 (2013)
39. J Kuhn, R Stemmer, F Kapteijn, S Kjelstrup, J Gross *J. Membr. Sci.* **330** 388 (2009)
40. J C Maxwell *Philos. Trans. R. Soc. London* **157** 49 (1867)

41. J Stefan *Sitzber. Akad. Wiss. Wien.* **63** 63 (1871)
42. A Heintz, W Stephan *J. Membr. Sci.* **89** 143 (1994)
43. A Heintz, W Stephan *J. Membr. Sci.* **89** 153 (1994)
44. U K Ghosh, N C Pradhan, B Adhikari *J. Membr. Sci.* **272** 93 (2006)
45. P Schaetzel, C Vauclair, G Luo, Q T Nguyen *J. Membr. Sci.* **191** 103 (2001)
46. P Sukitpaneenit, T-S Chung, L Y Jiang *J. Membr. Sci.* **362** 393 (2010)
47. B Smitha, D Suhanya, S Sridhar, M Ramakrishna *J. Membr. Sci.* **241** 1 (2004)
48. F Lipnizki, G Trägårdh *Sep. Purif. Rev.* **30** 49 (2001)
49. P Shao, R Y M Huang *J. Membr. Sci.* **287** 162 (2007)
50. V Soni, J Abildskov, G Jonsson, R Gani *Comput. Chem. Eng.* **33** 644 (2009)
51. P Izák, L Bartovská, K Friess, M Šípek, P Uchytil *Polymer* **44** 2679 (2003)
52. C Zeng, J Li, P Li, T Chen, Y Lin, D Wang, C Chen *Chem. Eng. Sci.* **61** 1892 (2006)
53. M Mujiburohman, K A Mahdi, A Elkamel *J. Membr. Sci.* **381** 1 (2011)
54. S Jeck, P Scharfer, M Kind *J. Membr. Sci.* **417–418** 154 (2012)
55. A M Polyakov *Krit. Tekhnologii. Membrany* (24) 29 (2004)
56. A M Polyakov, S A Solov'ev *Krit. Tekhnologii. Membrany* (30) 22 (2006)
57. J P G Villaluenga, A Tabe-Mohammadi *J. Membr. Sci.* **169** 159 (2000)
58. M I Bessonov, M M Koton, V V Kudryavtsev, L A Laius *Poliimidy — Klass Termostoikikh Polimerov* (Polyimides as a Class of Heat-Resistant Polymers) (Leningrad: Nauka, 1983)
59. A L Rusanov *Russ. Chem. Rev.* **48** 62 (1979)
60. C E Sroog *Prog. Polym. Sci.* **16** 561 (1991)
61. A Cano-Odena, P Vandezande, D Fournier, W Van Capm, F E Du Prez, I F J Vankelecom *Chem. – Eur. J.* **16** 1061 (2010)
62. S Darvishmanesh, J Degrève, B Van der Bruggen *Ind. Eng. Chem. Res.* **49** 9330 (2010)
63. Y Yin, O Yamada, K Tanaka, K-I Okamoto *Polym. J.* **38** 197 (2006)
64. N Asano, M Aoki, S Suzuki, K Miyatake, H Uchida, M Watanabe *J. Am. Chem. Soc.* **128** 1762 (2006)
65. H Ohya, V V Kudryavtsev, S I Semenova *Polyimide Membranes* (Tokyo: Gordon and Breach, 1996)
66. W J Koros, G K Fleming, S M Jordan, T H Kim, H H Hoehn *Prog. Polym. Sci.* **13** 399 (1988)
67. Yu V Kostina, G N Bondarenko, A Yu Alent'ev, Yu P Yampol'skii *Polym. Sci., Ser. A* **49** 77 (2007) [*Vysokomol. Soedin., Ser. A* **49** 96 (2007)]
68. A Alentiev, Yu Yampolskii, Ju Kostina, G Bondarenko *Desalination* **199** 121 (2006)
69. S Xiao, R Y M Huang, X Feng *Polymer* **48** 5355 (2007)
70. K Simons, K Nijmeijer, J G Sala, H van der Werf, N E Benes, T J Dingemans, M Wessling *Polymer* **51** 3907 (2010)
71. A B Yaroslavtsev, Yu P Yampolskii *Mendeleev Commun.* **24** 319 (2014)
72. Y Hirayama, T Yoshinaga, S Nakanishi, Y Kusuki, in *Polymer Membranes in Gas and Vapor Separation* (Eds B D Freeman, I Pinnau) (Washington, DC: The American Chemical Society, 1999) p. 194
73. K Zhou, Q G Zhang, G L Han, A M Zhu, Q L Liu *J. Membr. Sci.* **448** 93 (2013)
74. N D Hilmioglu, S Tulbentci *Desalin. Water Treat.* **48** 191 (2012)
75. Y Tang, N Widjojo, G M Shi, T-S Chung, M Weber, C Maletzko *J. Membr. Sci.* **415–416** 686 (2012)
76. C V Prasad, H Sudhakar, B Y Swamy, G V Reddy, C L N Reddy, C Suryanarayana, M N Prabhakar, M C S Subha, K C Rao *J. Appl. Polym. Sci.* **120** 2271 (2011)
77. Z Qiao, Y Wu, X Li, J Zhou *Fluid Phase Equilib.* **302** 14 (2011)
78. J Zuo, G M Shi, S Wei, T-S Chung *ACS Appl. Mater. Interfaces* **6** 13874 (2014)
79. P Boutikos, C S M Pereira, V M T M Silva, A E Rodrigues *Sep. Purif. Technol.* **127** 18 (2014)
80. M Omidali, A Raisi, A Aroujalian *Chem. Eng. Process.* **77** 22 (2014)
81. A M Sajjan, M Y Kariduraganavar *J. Membr. Sci.* **438** 8 (2013)
82. M Fathizadeh, A Aroujalian, A Raisi, M Fotouhi *Desalination* **314** 20 (2013)
83. C-L Lai, Y-J Fu, J-T Chen, Q-F An, K-S Liao, S-C Fang, C-C Hu, K-R Lee *Sep. Purif. Technol.* **100** 15 (2012)
84. P S Rachipudi, M Y Kariduraganavara, A A Kittur, A M Sajjan *J. Membr. Sci.* **383** 224 (2011)
85. P Das, S K Ray, S B Kuila, H S Samanta, N R Singha *Sep. Purif. Technol.* **81** 159 (2011)
86. O Bakhtiari, S Mosleh, T Khosravi, T Mohammadi *Sep. Sci. Technol.* **46** 2138 (2011)
87. M M Teoh, T-S Chung, K Y Wang, M D Guiver *Sep. Purif. Technol.* **61** 401 (2008)
88. L Y Jiang, T-S Chung, R Rajagopalan *Chem. Eng. Sci.* **63** 204 (2008)
89. Y Wang, L Jiang, T Matsuura, T S Chang, S H Goh *J. Membr. Sci.* **318** 217 (2008)
90. J-H Kim, B-J Chang, S-B Lee, S Y Kim *J. Membr. Sci.* **169** 185 (2000)
91. Y Xu, C Chen, J Li *Chem. Eng. Sci.* **62** 2466 (2007)
92. Y Xu, C Chen, P Zhang, B Sun, J Li *J. Chem. Eng. Data* **51** 1841 (2006)
93. C-L Li, K-R Lee *Polym. Int.* **55** 505 (2006)
94. M-Y Teng, C-L Li, K-R Lee, J-Y Lai *Desalination* **193** 144 (2006)
95. N L Le, Y Wang, T-S Chung *J. Membr. Sci.* **415–416** 109 (2012)
96. X Qiao, T-S Chung *Ind. Eng. Chem. Res.* **44** 8938 (2005)
97. Z Huang, H-m Guan, W-l Tan, X-Y Qiao, S Kulprathipanja *J. Membr. Sci.* **276** 260 (2006)
98. V S Praptowidodo *J. Mol. Struct.* **739** 207 (2005)
99. G Li, W Zhang, J Yang, X Wang *J. Colloid Interface Sci.* **306** 337 (2007)
100. Q Zhao, J Qian, Q An, Z Zhu, P Zhang, Y Bai *J. Membr. Sci.* **311** 284 (2008)
101. C L Hsueh, J F Kuo, Y H Huang, C C Wang, C Y Chen *Sep. Purif. Technol.* **41** 39 (2005)
102. X Qiao, T-S Chung *AIChE J.* **52** 3462 (2006)
103. A Yu Pulyalina, G A Polotskaya, I G Suschenko, T K Meleshko, L M Kalyuzhnaya, A M Toikka *Desalin. Water Treat.* **14** 158 (2010)
104. A Yu Pulyalina, G A Polotskaya, L M Kalyuzhnaya, I G Sushchenko, T K Meleshko, A V Yakimanskii, M V Chislov, A M Toikka *Russ. J. Appl. Chem.* **84** 840 (2011) [*Zh. Prikl. Khim.* **84** 810 (2011)]
105. L Y Jiang, T S Chung *J. Membr. Sci.* **346** 45 (2010)
106. A Pulyalina, G Polotskaya, M Goikhman, I Podeshvo, L Kalyuzhnaya, M Chislov, A Toikka *J. Appl. Polym. Sci.* **130** 4024 (2013)
107. Y K Ong, H Wang, T-S Chung *Chem. Eng. Sci.* **79** 41 (2012)
108. A Yu Pulyalina, A M Toikka, G A Polotskaya *Petrol. Chem.* **54** 573 (2014) [*Membr. Membr. Tekhnol.* **4** 140 (2014)]
109. R Kreiter, D P Wolfs, C W R Engelen, H M van Veen, J F Vente *J. Membr. Sci.* **319** 126 (2008)
110. D W Mangindaan, G M Shi, T-S Chung *J. Membr. Sci.* **458** 76 (2014)
111. X Qiao, T-S Chung, K P Pramoda *J. Membr. Sci.* **264** 176 (2005)
112. D Sun, P Yang, L Li, H-H Yang, B-B Li *Korean J. Chem. Eng.* **31** 1877 (2014)

113. J Kujawski, A Rozicka, M Bryjak, W Kujawski *Sep. Purif. Technol.* **132** 422 (2014)
114. W Liu, S-L Ji, H-X Guo, J Gao, Z-P Qin *J. Appl. Polym. Sci.* **131** Art. No. 40004 (2014)
115. A Rozicka, J Niemistö, R L Keiski, W Kujawski *J. Membr. Sci.* **453** 108 (2014)
116. D Sun, B-B Li, Z-L Xu *Desalination* **322** 159 (2013)
117. J Niemistö, W Kujawski, R L Keiski *J. Membr. Sci.* **434** 55 (2013)
118. S Claes, P Vandezande, S Mullens, K De Sitter, R Peeters, M K Van Bael *J. Membr. Sci.* **389** 265 (2012)
119. K-P Chao, V-S Wang, P Wang, T-Y Wang *Polym. Test.* **29** 939 (2010)
120. S Claes, P Vandezande, S Mullens, P Adriaensens, R Peeters, F H J Maurer, M K Van Bael *J. Membr. Sci.* **389** 459 (2012)
121. J R González-Velasco, C López-Dehesa, J A González-Marcos *J. Appl. Polym. Sci.* **90** 2255 (2003)
122. Y-H Chang, J-H Kim, S-B Lee, H-W Rhee *J. Appl. Polym. Sci.* **77** 2691 (2000)
123. M Krea, D Roizard, N Moulai-Mostefa, D Sacco *J. Membr. Sci.* **241** 55 (2004)
124. B-J Chang, Y-H Chang, D-K Kim, J-H Kim, S-B Lee *J. Membr. Sci.* **248** 99 (2005)
125. X Jiang, J Gu, Y Shen, S Wang, X Tian *Desalination* **265** 74 (2011)
126. Z W Song, J M Zhu, L Y Jiang *J. Membr. Sci.* **472** 77 (2014)
127. K Y Jee, Y T Lee *J. Membr. Sci.* **456** 1 (2014)
128. S Li, F Qin, P Qin, M N Karim, T Tan *Green Chem.* **15** 2180 (2013)
129. R Konietzny, T Koschine, K Rätzke, C Staudt *Sep. Purif. Technol.* **123** 175 (2014)
130. J Holtbruegge, M Wierschem, S Steinruecken, D Voss, L Parhomenko, P Lutze *Sep. Purif. Technol.* **118** 862 (2013)
131. S Maji, S Banerjee *J. Membr. Sci.* **360** 380 (2010)
132. M Rezakazemi, M Iravaninia, S Shirazian, T Mohammadi *Polym. Eng. Sci.* **53** 1494 (2013)
133. N R Singha, S K Ray *Sep. Purif. Technol.* **45** 2298 (2010)
134. W Xu, D R Paul, W J Koros *J. Membr. Sci.* **219** 89 (2003)
135. K-i Okamoto, H Wang, T Ijyuin, S Fujiwara, K Tanaka, H Kita *J. Membr. Sci.* **157** 97 (1999)
136. J Fang, K Tanaka, H Kita, K-i Okamoto *Polymer* **40** 3051 (1999)
137. H Wang, T Ugomori, Y Wang, K Tanaka, H Kita, K-i Okamoto, Y Suma *J. Polym. Sci., Part B: Polym. Phys.* **38** 1800 (2000)
138. H Wang, T Ugomori, K Tanaka, H Kita, K-i Okamoto, Y Suma *J. Polym. Sci., Part B: Polym. Phys.* **38** 2954 (2000)
139. M Schleiffelder, C Staudt-Bickel *React. Funct. Polym.* **49** 205 (2001)
140. L Wang, Z Zhao, J Li, C Chen *Eur. Polym. J.* **42** 1266 (2006)
141. C P Ribeiro Jr, B D Freeman, D S Kalika, S Kalakkunnath *Ind. Eng. Chem. Res.* **52** 8906 (2013)
142. Yu P Kuznetsov, S V Kononova, E V Kruchinina, K A Romashkova, V M Svetlichnyi, V A Molotkov *Russ. J. Appl. Chem.* **74** 1338 (2001) [*Zh. Prikl. Khim.* **74** 1302 (2001)]
143. G A Polotskaya, Yu P Kuznetsov, M Ya Goikhman, I V Podeshvo, T A Maricheva, V V Kudryavtsev *J. Appl. Polym. Sci.* **89** 2361 (2003)
144. A Yu Pulyalina, G A Polotskaya, K Yu Veremeychik, M Ya Goikhman, I V Podeshvo, A M Toikka *Fuel Process. Technol.* **139** 178 (2015)
145. G A Polotskaya, T K Meleshko, I G Sushchenko, A V Yakimansky, A Yu Pulyalina, A M Toikka, Z Pientka *J. Appl. Polym. Sci.* **117** 2175 (2010)
146. A Yu Pulyalina, G A Polotskaya, L M Kalyuzhnaya, N N Saprykina, I G Sushchenko, T K Meleshko, A M Toikka *Polym. Sci., Ser. A* **52** 856 (2010) [*Vysokomol. Soedin., Ser. A* **52** 1466 (2010)]
147. H M van Veen, Y C van Delft, B Bongers, C W R Engelen, P P A C Pex, in *The 10th Aachen Membrane Colloquium. (Proceedings), Aachen, 2005* p. 1
148. B Bettens, A Verhoef, H M van Veen, C Vandecasteele, J Degreve, B Van der Bruggen *Comput. Chem. Eng.* **34** 1775 (2010)
149. A Wolińska-Grabczyk *J. Membr. Sci.* **282** 225 (2006)
150. Y X Bai, J W Qian, H B Sun, Q F An *J. Membr. Sci.* **279** 418 (2006)
151. J Frahn, G Malsch, H Matuschewski, U Schedler, H-H Schwarz *J. Membr. Sci.* **234** 55 (2004)