High-Selectivity Polysiloxane Membranes for Gases and Liquids Separation (A Review)

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Abstract—The most promising approaches to making polysiloxane-based membranes more selective are considered. These approaches can be subdivided into three groups: (1) development of new membrane materials by copolymerization, (2) modification of the polysiloxane chain (in the backbone and pendant chains), and (3) development of mixed matrix membranes. All the three approaches are subjected to a critical analysis, and conclusions are made on the prospects for the development of high-selectivity materials and high-performance membranes based on them. The data are presented from the viewpoint of applied aspects of polysiloxane-based membranes.

Keywords: silicone rubbers, polydimethylsiloxane, membranes, membrane technology, pervaporation, gas separation, vapor separation, polyorganosiloxanes

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Membrane technologies are widely used in separation of gaseous and liquid media, in particular, in oil refining, gas processing, and petroleum chemistry [1–4]. The examples of such separations are nitrogen separation from air [5–7], helium separation from natural gas [8, 9], hydrogen separation from process streams [10–13], trapping of highly volatile organic compounds from air media [1, 14], etc.

Polysiloxanes (silicone rubbers) as polymeric membrane materials have found wide use in commercial membrane productions [2, 15]. These materials are mainly used for such processes as gas separation [16], vapor separation [17], and pervaporation [4].

In nonporeous membrane materials, the transport of gases and vapors occurs by the dissolution–diffusion mechanism [18]. Siloxane rubbers belong to the group of membrane materials for which the solubility factor makes the decisive contribution to the membrane selectivity. Thus, polysiloxane membranes will mainly transmit readily condensing compounds (C3+ hydrocarbons, alcohols, low-boiling organic compounds, etc.), which often are bulky organic molecules.

The best studied and the most widely used polysiloxane is polydimethylsiloxane (PDMS), a highly permeable material [19–22]. This property is caused by high flexibility of the polysiloxane chain (T_g(PDMS) = −125°C [23, 24]). At room temperature, PDMS is in the hyperelastic state; therefore, its chemical cross-linking is required to ensure the required mechanical properties [25, 26]. On the other hand, PDMS demonstrates relatively low selectivity of separating gases, e.g., air components or lower hydrocarbons (the ideal selectivity is as follows: CO_2/N_2 = 9.5 [27] and n-C_4H_10/CH_4 = 17 (for 3% n-C_4H_10/97% CH_4 binary mixture, 5 [21]). Therefore, much attention is paid to the development of materials and membranes based on polysiloxanes with enhanced separation characteristics [16, 28–31]. Both chemical (cross-linking [32], copolymerization [33], modification of the backbone [34] and pendant chains [31], etc.) and physical methods of polysiloxane design (preparation of mixed matrix membranes with zeolites [35, 36], activated carbons [37], silicalites [38], etc.) are used for the development of high-selectivity membrane materials based on polysiloxanes.
Here we consider the most promising approaches to enhancing the selectivity of polysiloxane-based membranes and the main fields of their use in membrane technology.

**DEVELOPMENT OF NEW MEMBRANE MATERIALS BY COPOLYMERIZATION**

Copolymerization of various monomers is one of widely used approaches to the design of membrane materials. Modern synthetic possibilities allow the development and synthesis of block copolymers with a wide spectrum of physical and chemical properties. The ratio of the organic and inorganic blocks determines the membrane properties of a material (permeability, selectivity, mechanical properties). Such approach allows preparation of new membrane materials with improved properties. For example, the presence of rigid block based on glassy polymers in the siloxane chain improves the mechanical properties and film-forming ability with the preservation of high permeability coefficients [39–41]. Copolymerization of siloxanes is also performed jointly with polycarbonates [42], polystyrene [33], poly(alkyl methacrylates) [30], polyesters [43], and polysilphenylenesiloxane [44, 45]; however, the mutual compatibility of the polysiloxane and hydrocarbon chains is limited. As noted by Raigorodskii et al. [40], thermodynamic and mechanical incompatibility of organic and organosilicon blocks causes aggregation of each of them into separate phases and formation of a two-phase morphology, which can lead to phase segregation. For example, Beckman and Teplyakov note [46] that a blend of two continuous phases in polyvinyltrimethylsilane (PVTMS)–PDMS block copolymers can be formed only at the PDMS content in the interval from 25 to 40 vol %. At the PDMS content higher than 40 vol %, the system is a dispersion of platelike PVTMS particles in a PDMS medium. At the PDMS content of the block copolymer lower than 25 vol %, the two-phase system consists of needle-like PDMS particles dispersed in PVTMS.

In preparation of polyorgano–polysiloxane block copolymers, the initial organosilicon compounds can be diverse: cyclosiloxanes, unsaturated siloxanes, and silicon- and carbofunctional siloxanes; they can also contain various active groups. Such copolymers are prepared by polymerization, polymerization–polycondensation, and polycondensation methods [40].

**Scheme 1.** Synthesis of polystyrene–polysiloxane copolymers [47].

\[
C_4H_9Li + m\text{CH}=\text{CH} \rightarrow C_4H_9(CH_2CH)_{m-1}CH_2\text{CHLi}
\]

\[
C_4H_9(CH_2CH)_{m}Li \xrightarrow{+D_3, D_4} C_4H_9(CH_2CH)_{m}(\text{SiOMe}_2)_nLi
\]

\[
+\text{Me}_2\text{SiCl}_2 \rightarrow \text{LiCl}
\]

\[
C_4H_9(CH_2CH)_{m}(\text{SiOMe}_2)_n\text{SiMe}_2(\text{OSiMe}_2)_p(CHCH_2)_xC_4H_9
\]

\[
D_3 \text{ is hexamethylocyclotrisiloxane, and } D_4 \text{ is octamethylocyclotetrasiloxane.}
\]
For example, polystyrene–polysiloxane was prepared by living polymerization (Scheme 1) [47].

Introduction of 40 mol % polystyrene into PDMS by block polymerization allowed the separation factor to be increased by a factor of 7.5 and the permeability in pervaporation separation of a 0.05 wt % benzene/water mixture, by 20% [33]. Uragami et al. [33] note that such effect is caused by an increase in the benzene sorption in the block copolymer compared to pure PDMS.

Matsumoto et al. [48] described multiblock copolymers containing units of PDMS and aromatic polyamides (the PDMS amount in the copolymer was varied from 26 to 75 wt %). The oxygen and nitrogen permeability coefficients of the polymer films obtained increased with an increase in the fraction of siloxane blocks. At 75% siloxane content of the copolymer, the oxygen permeability coefficient was 224 Barrer and the oxygen/nitrogen selectivity was 2.3, whereas for the copolymer containing 46% siloxane the oxygen permeability coefficient was 41 Barrer and the oxygen/nitrogen selectivity was 2.4. Introduction of siloxane blocks into the rigid-chain polyamide increases the segmental mobility of the chain, which, in turn, increases the permeability coefficient.

Siloxane block copolymers have a number of advantages over traditional silicone rubbers due to good mechanical and film-forming properties. Composite gas-separation membranes with the selective layer based on a block copolymer of α,ω-bis(diethylamino)-diorganosiloxane oligomer with phenylsilsesquioxane (Lesto-sil™), synthesized at Polimersintez (Vladimir, Russia), were prepared at the Vladipor Scientific and Technical Center (Vladimir, Russia) [49–52]. A hollow-fiber membrane of polysiloxane–polycarbonate block copolymer (Karbosi™) synthesized at the State Research Institute of Chemistry and Technology of Organoelement Compounds (Moscow, Russia) was developed at Khimvolokno Production Association (Mytishchi, Moscow oblast, Russia) [51, 52]. A block copolymer of oligoarylate with oligodimethylsiloxane, named Silar, was also synthesized [52, 53]. Membranes based on these copolymers are presently produced by Vladipor; this is the series of MDK gas-separation composite membranes. These membranes exhibit high, compared to PDMS, separation characteristics, and their preparation does not involve chemical cross-linking [52]. Borisov et al. [44] have shown that MDK-3 membrane (Vladipor) with the selective layer made of polydimethylsiloxane–polyphenylsilsesquioxane copolymer exhibits higher separation factor in thermopervaporation separation of a 1 wt % n-butanol–water mixture (11.5) compared to the Pervatech PDMS commercial membrane with the PDMS-based selective layer (7.8), developed by Pervatech (Netherlands) for organophilic pervaporation.

**MODIFICATION OF POLYSILOXANES IN THE BACKBONE AND PENDANT CHAINS**

Chemical modification of polysiloxanes is performed in the course of polymerization or polymer-analogous transformations. This approach is aimed at incorporation of hydrocarbon or functionalized fragments into the backbone [31, 54–58] or pendant chains [29, 31, 56, 59] of polysiloxane.

**Backbone modification.** Such modification of the polymethylsiloxane backbone is performed in the course of polymerization of the corresponding cyclosiloxanes by ring opening (Scheme 2) [57, 60, 61] or by hydrolytic polycondensation (Scheme 3) [62–64].

\[
\text{Me}_2\text{Si} \quad \text{Me} \quad \text{Me} \\
\text{O} \quad \text{SiMe}_2 \\
(\text{CH}_2)_n \\
\text{Bu}_4\text{NOH} \quad \text{or CF}_3\text{SO}_3\text{H} \\
\text{Me} \quad \text{Me} \\
\text{Si} \quad \text{O} \quad \text{H} \\
\text{Me} \quad \text{Me} \\
\text{Me} \\
\text{Me}
\]

**Scheme 2.** Scheme of ring opening polymerization of cyclocarbosiloxane with \( n \)-methylene groups [57].
Studies on the synthesis of cyclocarbosiloxanes and polydimethylsilalkylenes and on transport properties of membranes based on them are relatively few [31, 55–58]. Borisov et al. [34] studied the gas-transport properties of polydimethylsildimethylene- and polydimethylsiltrimethylenedimethylsiloxane. Introduction of three methylene fragments into the PDMS backbone leads to a decrease in the \( \text{n-butane} \) permeability coefficient from 14000 to 6600 Barrer\(^3\) with a simultaneous increase in the ideal \( \text{n-butane} / \text{methane} \) separation selectivity from 11 to 15. Thus, variation of the length of the hydrocarbon fragment in the polycarbosiloxane backbone can be used for developing a more selective membrane material for separation of lower hydrocarbons. Stern et al. [31] studied the influence of the structure of the hydrocarbon fragment in the polydimethylsiloxane backbone. They examined the polymers containing linear aliphatic fragments (2, 6, 8 methylene groups) and phenylene groups with the silicon atoms in the \( \alpha \)- and \( \beta \)-positions. They note that introduction of bulky hydrocarbon fragments into the polysiloxane backbone leads to a decrease in the gas permeability of the polymers (the permeability coefficient decreased from 933 to 11 Barrer for oxygen and from 4553 to 64 Barrer for carbon dioxide) and to an increase in the separation selectivity (the oxygen/nitrogen separation selectivity increased from 2.0 to 3.3). However, these approaches suggest multistep synthesis of the starting monomers [65]. In addition, e.g., cyclic carbosiloxanes are prepared in a low yield, which makes topical further search for optimum monomer synthesis procedures [66].

**Pendant chain modification.** Polyorganosiloxanes with various pendant substituents can be prepared both by polymerization [67] and by polymer-analogous transformations [68–70]. Such approaches as hydrolytic polycondensation were used (Scheme 4). The polycondensation mechanism in the presence of water is presented in more detail in Scheme 5 [67]. It should be noted that this procedure is a multistep synthesis from chlorosilanes to carbofunctional organosilicon compounds [67].

The second procedure for preparing polysiloxanes substituted in the pendant chain, suggested for the first time in [29], consists in modification of the siloxane chain by polymer-analogous transformations. Such substituted

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\(^3\) Here and hereinafter, the gas permeability coefficient was measured at 30°C and a pressure tending to zero (unless otherwise indicated).
polysiloxanes are prepared by hydrosilylation, namely, by the reaction of polymethylhydrosiloxane (PMHS) with 1-alkene in the presence of a Pt-containing catalyst (Karstedt or Speier catalyst) (Scheme 6) [63].

Stern et al. [31] studied the gas-transport properties of polymethylsiloxanes with different pendant groups, including the methyl, ethyl, propyl, octyl, and phenyl groups. The glass transition point increased with an increase in the substituent volume, which means that the polymer chain mobility decreases. As a consequence, the oxygen permeability coefficient decreased in the series of substituents methyl–ethyl–propyl–octyl–phenyl: 933–312–383–190–32 Barrer, respectively. The oxygen/nitrogen selectivity increased from 2.0 to 3.1 with an increase in the pendant substituent volume [31].

Lee et al. [56] studied how the polymer pendant chain structure influences the oxygen and nitrogen permeability of silicone polymers of the general formula (MeRSiO)_x, where R is alkyl, aryl, or CH_2CH_2CF_3. As they found, with an increase in the alkyl group size from C_1 to C_8, the permeability coefficient appreciably decreased (for O_2, from 78 to 20 Barrer), whereas the O_2/N_2 selectivity increased (from 2.10 to 2.29). Introduction of the benzene ring into the polysiloxane pendant chain led to a decrease in the permeability coefficient by more than an order of magnitude (2.5 Barrer) and to an increase in the O_2/N_2 selectivity to 2.98 compared to linear alkyl substituents.

Ashworth et al. [59] studied how the pendant ester group influences the gas permeability of polysiloxane polymers. As they showed, with an increase in the content of ester groups from 0 to 24.1% the CO_2 solubility coefficient increased. As a consequence, the CO_2/CH_4 selectivity increased from 3.14 to 3.92.

**Scheme 4.** Preparation of polyorganosiloxanes by polycondensation.

\[ \rho[R_2SiO]_4 + AB \xrightarrow{\text{cat}} AO[R_2SiO]_d B + [R_2SiO]_2 \]

\[ AB = H_2O, R_3SiOSi(X_2)R_4, R_nSiX_{4-n}; R = \text{H, aliphatic, aromatic, carbofunctional substituent; } n = 0–3. \]

**Scheme 5.** Polycondensation mechanism.

\[ qR_nSiX_{4-n} + zR^1_mSiX_{4-n} + [\text{H}_2O] \xrightarrow{\text{cat}} [R_nSi(OH)]_{4-n-p} O_{p/2} [R^1_mSi(OH)]_{4-m-p} O_{p/2} \]

\[ \xrightarrow{\text{cat}} [R_nSi(OH)]_{(4-n)/2} q[R^1_mSiO]_{(4-m)/2} z \]

**Scheme 6.** Synthesis of modified polymethylsiloxane.
In [71], we suggested performing the modification of polymethylhydrosiloxane with 1-alkene and cross-linking with 1,7-octadiene in situ in the presence of Karstedt catalyst. Such approach allowed preparation of membranes from polyalkylmethylsiloxanes in one step. Performing the modification and cross-linking by hydrosilylation allows also using a single catalyst, which improves the economic efficiency of this approach. The simplicity of the suggested procedure allowed us to study in our subsequent works how various cross-linking agents influence the gas-transport properties of membranes based on polyoctylmethylsiloxane (POMS) [72] and polydecylmethylsiloxane [73]. As we showed, an increase in the length of the cross-linking agent, divinyltetramethyldisiloxane–PDMS ($M_n = 25000$ g mol$^{-1}$), leads to a decrease in the ideal $n$-butane/methane selectivity from 26 to 22 and to an increase in the permeability coefficient (from 9600 to 9800 Barrer at the pressure over the membrane of 0.8 bar) [72].

**Chemical cross-linking.** The majority of polysiloxanes are viscous liquids at room temperature. To prepare continuous membranes with the required mechanical characteristics, chemical cross-linking of the polymer via functional groups is performed. The most widely used procedure is cross-linking with alkoxysilanes via terminal silanol groups of the polymer in the presence of tin catalysts [29, 34, 59, 74–76]. The use of functional alkoxysilanes R'Si(OR)$_3$ (for example, R' is vinyl [75] or phenyl [74] groups) allows preparation of PDMWS with different levels of cross-linking density, glass transition point, hydrophobicity, and transport properties. For example, in [76] an increase in the tetraethoxysilane content of the reaction mixture with PDMS from 0 to 30 wt % leads to a decrease in the oxygen permeability coefficient from 640 to 185 Barrer (at 0.5 bar). It is worth noting that the properties of a membrane obtained by cross-linking depend not only on the cross-linking agent type but also on the cross-linking conditions (temperature, solvent, drying conditions, etc.) [77–79]. For example, Berean et al. [80] attribute a decrease in the methane permeability coefficient of PDMS from 1000 to 480 Barrer, observed when the cross-linking temperature was increased from 75 to 100°C, to a decrease in the fraction of the void volume in the polymer (at 0.4 bar).

**DEVELOPMENT OF MIXED MATRIX MEMBRANES**

Mixed matrix membranes (MMMs) are two-phase systems. A continuous matrix of a polymer membrane material is filled with dispersed, most frequently inorganic, particles. Introduction of such particles allows altering the transport properties of a membrane material, e.g., enhancing the separation selectivity or increasing the void volume of the polymer matrix [81]. It should be noted, however, that, when preparing mixed matrix membranes, it is necessary to solve a number of problems associated with the synthesis and disintegration of particles of submicron or nanometer size, improvement of their compatibility with the polymer matrix (for uniform distribution in the matrix volume), and application of a thin flawless selective layer of the hybrid material onto a porous support.

In the first studies on the development of mixed matrix membranes based on a siloxane polymer, molecular sieves were used as fillers. Among them, the most widely used are activated zeolites (A, Y, ZSM-5, ZIF-8) [35, 36, 82–84]. Such additives allow forming additional sorption sites in the polymer matrix, which, in turn, enhances the selectivity of hydrocarbon transport through the membrane. Incorporation of a small volume fraction of inorganic fillers into a polymer matrix can considerably increase the overall separation efficiency, as predicted by the Maxwell model [85–87]. Maxwell equation (1) allows estimation of the resultant permeability of a mixed matrix membrane ($P_{\text{eff}}$) from the fraction of inorganic particles ($\Phi_d$) in the polymer and permeability of the dispersed ($P_d$) and continuous ($P_c$) phases [85]:

$$\frac{1}{P_{\text{eff}}} = \frac{1}{P_c} + \frac{\Phi_d}{P_d} + \frac{1}{P_c} + \frac{\Phi_d}{P_d}$$

A pioneering study was performed by Paul and Kemp [88] and extended by Kulprathipanja et al. [89]. According to [88], introduction of 5A zeolite into silicone rubber did not improve the ability of the polymer for CO$_2$/CH$_4$ separation. They also noted that introduction of particles into a silicone rubber matrix considerably increased the...
delay time in measuring the diffusion coefficient. In their opinion, this negatively influences the membrane permeability. The first success (considerable increase in the O₂/N₂ and CO₂/CH₄ selectivity) was reached for membranes based on polydimethylsiloxane and ethylene–propylene–diene rubber with zeolite additions [90]. Duval et al. [90] showed that zeolites (silicalite-1, 13X, and KY) largely improved the characteristics of rubber polymers in CO₂/CH₄ separation. Jia et al. [86] reported an increase in the O₂ permeability (from 571 to 655 Barrer at a pressure of 1 bar) and O₂/N₂ selectivity (from 2.14 to 2.92) on introducing silicalite-1 into silicone rubber. According to [35], introduction of ZIF-8 increases the selectivity in separation of a propane (20%)–nitrogen (80%) mixture at a pressure over the membrane of 2 bar from 14.5 (PDMS) to 21 (PDMS/20% ZIF-8) but decreases the permeability from 155 to 98 GPU (gas permeation units). As shown in [28, 37], with an increase in the activated carbon content of the initial POMS matrix, its gas permeability increases and the n-C₄H₁₀/CH₄ separation selectivity increases. The butane permeability increases with an increase in the feed pressure, and the selectivity passes through a maximum at the feed pressure of 20–30 bar. Tantekin-Ersolmaz et al. [36] observed a similar effect of a decrease in the membrane permeability with an increase in the inorganic component/polymer ratio for PDMS membranes filled with zeolites. Haesook et al. [91] introduced silica nanoparticles into the a selective layer of PDMS membranes on a polysulfone support. This allowed the propylene/nitrogen separation factor to be increased from 5.2 to 7.3. Efficient interaction of polysiloxanes and zeolites is mainly attributed in [91] to the flexibility of the polymer chain.

Recently there has been a great deal of interest in introduction of framework structures as a dispersed phase in the development of mixed matrix membranes. For example, polyhedral oligomeric silsesquioxanes (POSSs) were widely used for this purpose [92–97]. In contrast to common fillers, POSSs have a particle size of approximately 2 nm and a flexible structure. In addition, POSS can be functionalized with various groups bonded to external silicon atoms. Specifically diverse functional groups and good compatibility with polymers allowed POSS as an additive to find use in the development of laboratory membrane samples for pervaporation [92–94] and gas separation [95]. This is primarily associated with the fact that POSS in this case acts as both an additive and a cross-linking agent. Introduction of 40 wt % nanofillers based on POSS allowed the development of pervaporation membranes with enhanced levels of selectivity (7.5) and permeability (300 × 10³ Barrer for n-butanol) for separating 1 wt % n-butanol from water [92].

The transport properties of polysiloxane mixed matrix membranes are summarized in Table 1.

### Table 1. Effect of the dispersed phase on the gas transport properties of PDMS membranes

| Filler       | Gases                  | Gas separation selectivity | Permeability/permeability coefficient | References |
|--------------|------------------------|----------------------------|---------------------------------------|------------|
| ZIF-8 (10%)  | 20% C₃H₈/80% N₂        | 24                        | C₃H₈: 1000 GPU                        | [35]       |
| Silicalite-1 (40%) | CO₂ and N₂            | 12                        | CO₂: 5000 Barrer                      | [36]       |
| Silicalite-1 (50%) | CO₂ and CH₄       | 5.7                       | CO₂: 3150 Barrer                      | [86]       |
| Silicalite-1 (59%) | CO₂ and CH₄       | 30                        | CO₂: 1910 Barrer                      | [90]       |
| 5A (50%)    | CO₂ and CH₄            | 28                        | CO₂: 1800 Barrer                      | [90]       |
| Silica nanoparticles | 15% C₃H₈/85% N₂ | 7.5                       | C₃H₈: 75 GPU                          | [91]       |
| POSS        | C₃H₈ and CH₄           | 10                        | C₃H₈:10500 Barrer                     | [95]       |

1 Barrer = 1 × 10⁻¹⁰ cm³ cm⁻² s⁻¹ (cm Hg)⁻¹; 1 GPU=1 × 10⁻⁶ cm³ cm⁻² s⁻¹ (cm Hg)⁻¹.

### SEPARATION OF GASES AND VAPORS

Numerous gas-separation modules based on silicone rubber are used today on the pilot and commercial scale for the gas treatment and processing: Separex (UOP), Medal (Air Liquid), W.R. Grace, MTR, Permea (Air Products), and UBE Industries [4, 98, 99]. The main
suppliers of systems for membrane separation of organic vapor/air (gas) mixtures are MTR [100] and licensiates of the Helmholtz-Zentrum Geesthacht research center (HZG, former name GKSS): Borsig, SiHi, and Dalian Eurofilm [1]. The membrane separation systems supplied by these companies are mainly used in the production of polyolefins (separation of monomers), polyvinyl chloride (off-gas treatment), ethylene oxide, and vinyl acetate (ethylene separation); in storage terminals for crude oil and petroleum products (trapping of gasoline vapors from off-gases); at compressor stations for natural gas transportation (reduction of the concentration of C₃+ hydrocarbons)⁴⁵⁶; and at small chemical and pharmaceutical enterprises [101]. The first installation for organic vapor recuperation based on membrane technologies was put into operation by GKSS GS-module in 1989 at the gasoline repository, and by 1995 already 20 membrane installations with the productive capacity of 100–2000 m³ h⁻¹ were supplied to enterprises for organic vapor recuperation based on membrane [101]. MTR company uses in its membrane modules membranes based on perfluorinated polymeric silicone rubbers [102]. The advantage of such polymers is their high chemical durability [4]; they are characterized by decreased solubility coefficients of gaseous hydrocarbons and do not swell or degrade in contact with petroleum products [103].

PDMS is widely used in preparation of gas-separation membranes as a finishing coating eliminating flaws [5, 6, 8, 104]. Gas-transport properties of PDMS have been extensively studied. Much attention is paid in research papers to transport properties of silicone rubbers in separation of gases, including hydrocarbons. These properties were studied both for continuous films [27, 31, 105, 106] and for composite membranes [21, 107]. The permeability coefficients have been reported for the n-butane/methane pair: 930–1500 Barrer for methane and 7200–14000 Barrer for n-butane [27, 31, 105, 106]. The transport properties of PDMS-based systems were also studied as applied to binary mixtures containing n-butane and multicomponent mixtures simulating the natural gas composition. Unfortunately, a considerable decrease in the PDMS selectivity in separation of gas mixtures is observed. The n-butane/methane selectivity, compared to the ideal selectivity, decreases from 11 to 5 [21, 106] because of an increase in the methane permeability coefficient from 1200 to 1400 Barrer [106].

A commercial membrane based on polyoctylmethylsiloxane (POMS), developed in Germany in the GKSS-Forschungszentrum Geestacht GmbH research center (since 2010, Helmholtz-Zentrum Geestacht GmbH), has been actively studied in the past decades [21, 28, 37, 108, 109]. Because POMS membranes are successfully produced on the commercial scale, their preparation procedure is not described in open sources [37]. POMS, compared to PDMS, is characterized by higher selectivity to organic vapors, as found in experiments with pure substances and on separation of hydrocarbon mixtures [21, 110]. One of the first studies dealing with this polymer was the study by Schultz and Peinemann [21], who reported the properties of a composite POMS membrane. For example, a POMS-based membrane showed 2.4 times higher n-butane/methane separation selectivity (12), compared to a PDMS-based membrane (5), in separation of the binary mixture containing 3% n-butane at a pressure of 10 bar [21]. In [28, 37], POMS-based mixed matrix membranes were prepared by introducing activated carbon particles into the polymer matrix. As compared to composite membranes without filler, mixed matrix membranes exhibit somewhat higher separation selectivity [22 (POMS) and 25 (POMS-MMM)] and lower permeability in separation of a 5 vol % n-butane/methane binary mixture at a pressure of 10 bar [37].

Novel membrane materials, including siloxane polymers with modified chemical structure, also attract researchers’ attention. The effect of the pendant substituent (ethyl, propyl, hexyl, octyl, phenyl, 3-fluoropropyl) in the siloxane chain was studied in [31, 56]. Lee et al. [56] reported the O₂ and N₂ permeability coefficients of polysiloxanes, and Schultz and Peinemann [21] also studied the transport of hydrocarbons (methane, propane) and carbon dioxide. A later study [71] deals with the correlation between the structure and transport properties of polydecylmethylsiloxane. It should be noted that polydecylmethylsiloxane (PDecMS),

⁴ Dalian Eurofilm Industrial Ltd. Co, P.R.China, http://eurofilm.com.cn/en/product/?id=32 (addressed June 10, 2021).
⁵ Sterling SIHI GmbH. Gas separation by using membranes. http://www.sterlingsihi.com/ (addressed June 10, 2021).
⁶ BORSIG GmbH [electronic resource] / mt.borsig.de/en: BORSIG Membrane product GmbH. http://mt.borsig.de/en/products.html (addressed June 10, 2021).
compared to other polyalkylmethylsiloxanes (alkyl = hexyl, octyl), showed the highest ideal \( n \)-butane/methane selectivity (27). Later [111], the separation properties of polyalkylmethylsiloxanes in separation of an eight-component model mixture of hydrocarbons, simulating the casinghead gas composition, were reported. The PDecMS-based composite membrane on MFFK-1 microporous support surpassed commercial membranes MDK-3 (Vladipor, Russia) and POMS (HZG, Germany) in separation selectivity at comparable \( n \)-butane permeability [111]. In particular, the \( n \)-butane permeability was 850 GPU, and the \( n \)-butane/methane selectivity was 16.7. A promising continuation of that study is the development of hollow-fiber composite membranes [112–114]. The hollow-fiber membrane geometry allows intensification of the \( n \)-butane separation [115].

### SEPARATION OF LIQUIDS: PERVAPORATION

Separation of liquids by hydrophobic pervaporation is mainly performed using membranes based on polysiloxanes. This separation process is primarily aimed at removal of organic substances from wastewaters from various chemical, petrochemical, pharmaceutical, and other enterprises [116]. Pervaporation is also widely used in food industry (recovery of aroma components from fruit juices) [117] and in separation of fermentation products (alcohols) in biofuel production [118]. The majority of membranes intended for hydrophobic pervaporation are made of polysiloxanes and composites based on them. These membranes include Pervatech PDMS and POMS\(^7\), PERVAP 1070, 4060\(^8\), POMS, MDK-3, and MTR 100, 200 [120–123].

A study by Bennett et al. [29] was one of the first studies dealing with the effect of a pendant substituent on the pervaporation properties of composite polysiloxane membranes in recovery of organic compounds from water. Bennett et al. reported the results of pervaporation recovery of phenol, chloroform, pyridine, and methyl isobutyl ketone from their mixtures with water. Bennett et al. [29] studied a series of polymers with different pendant substituents (Table 2). As they showed, the separation selectivity is considerably enhanced with an increase in the sorption of the organic component and/or a decrease in the water transport. For example, in separation of a 5 wt % solution of phenol in water, the PDMS membrane flux with respect to phenol was \( 2.15 \times 10^{-11} \) m\(^2\) s\(^{-1}\), and the separation factor was 17.7. The siloxane membrane with the pyridine ring in the pendant chain (10% content of functional groups) showed the best transport properties: membrane flux with respect to phenol \( 5.57 \times 10^{-11} \) m\(^2\) s\(^{-1}\) and separation factor 31.8. Bennett et al. note that phenol interacts with basic groups of the membrane, which enhances both the throughput and selectivity of the membrane with respect to phenol.

For removing methyl tert-butyl ether from wastewater, Borisov et al. [124] considered polyalkylsiloxanes with

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\(^7\) Membranes, Pervatech. https://pervaporation-membranes.com/products/membranes/

\(^8\) Sulzer Chemtech. Membrane Technology. https://www.sulzer.com/-/media/files/products/process-technology/reaction_technology/brochures/membrane_technology.ashx
hexyl, octyl, and decyl pendant substituents, and also composite membranes based on them. The composite membrane based on polydecylmethylsiloxane, prepared in [124], showed the best characteristics (separation factor 310, total flux 0.82 kg m\(^{-2}\) h\(^{-1}\)) compared to the previous data [125–128]. Polydecylmethylsiloxane on MFFK-1 microfiltration support showed high selectivity in \(n\)-butanol recovery from water (2.8) [129].

Kujawska et al. [130] studied the pervaporation properties of Pervatech PDMS (Pervatech, Netherlands), Pervap 4060 (Sulzer Chemtech, Switzerland), and POMS (HZG, Germany) membranes in separation of binary mixtures of acetone, butanol, ethanol, and ethyl acetate with water. They noted correlation of the surface free energy of the membranes with the transport properties. The surface free energy decreases in the order Pervap 4060 > POMS > Pervatech, which leads to a decrease in the permeability with respect to the organic component and in the separation selectivity (Table 3).

The membranes based on PDMS modified with zeolites and inorganic salts appeared to be the best for the ethanol recovery [131–134]. For example, in separation of a 5 wt % aqueous ethanol solution at 50°C, the maximal separation factor for the PDMS-ZSM-5/PVDF membrane (30 wt % zeolite) was 14 at an ethanol flux of the order of 344 g m\(^{-2}\) h\(^{-1}\) [132]. For continuous PDMS films modified with NaCl and Al\(_2\)O\(_3\), the separation factors in separation of a 5 wt % aqueous ethanol solution at 30°C are 10–11 [131].

Recovery of aroma compounds from biological media is a separate direction in the membrane science. In most cases, aroma compounds are oxygenates (esters, aldehydes, ketones, alcohols) present in low concentrations in liquids of biological origin. Pervaporation is the most promising procedure for their recovery, because, as compared to traditional extraction, it does not require auxiliary substances contaminating the foodstuffs and requiring the regeneration and additional purification. Data are available on the recovery of aroma components from orange [135], grape [136], punica [137], strawberry [138], bilberry [139], and other juices, and also from beer [140] and alcohol-free wine [141] by pervaporation using polysiloxane-based membranes. These studies demonstrated both selective concentration of aroma components and high stability of siloxane membranes in various drinks. For example, Sun et al. [141], when preparing alcohol-free wine by pervaporation through a PDMS membrane, concentrated ethanol (content in the permeate up to 50 vol %) and aroma components (65–70 wt % passed into the permeate). They also note improvement of the alcohol-free product taste after pervaporation, compared to distillation, due to deeper removal of aroma compounds (tannins, esters, acids).

Studies dealing with the development of a process for producing biobutanol in a pervaporation membrane bioreactor (integrated fermentation–pervaporation process) can be considered as a separate group of studies. They are aimed at determination of the process parameters and development of novel membranes with high operation characteristics [44, 82, 92, 142, 143]. Introduction of POSS into a polysiloxane pervaporation membrane allows a simultaneous increase in the selectivity by a factor of 2.2 and in the permeability by a factor of 3.8, compared to the initial PDMS membrane [92]. Zhu et al. [144] note that, in butanol production in a pervaporation membrane bioreactor, introduction of fluorinated fragments into the material of polysiloxane membranes considerably reduces their plugging and enhances the stability of transport properties. The development of such membranes will allow passing to commercial implementation of the integrated fermentation–pervaporation process.

| Membrane      | Permeability, mol m\(^{-2}\) h\(^{-1}\) kPa\(^{-1}\) | Selectivity |
|---------------|-----------------------------------------------|-------------|
| acetone       | Pervap 4060 4.6  POMS 2.3  Pervatech 2.8      | Pervap 4060 0.8  POMS 0.6  Pervatech 0.4     |
| butanol       | 14 7.2 6.7                                          | 2.0 0.4 0.7                                          |
| ethanol       | 4.1 5.3 3.7                                          | 0.9 0.5 0.4                                          |
| ethyl acetate | 24.2 19.5 14.3                                      | 4.4 3.0 23                                          |

Table 3. Selectivity and permeability of Pervap 4060, POMS, and Pervatech membranes [130]
HIGH-SELECTIVITY POLYSILOXANE MEMBRANES

The prospects for commercial use of membrane separation are determined by the possibility of process implementation in small-size units and by low levels of power and resource consumption [145, 146]. Siloxane polymers exhibit high levels of permeability, heat resistance, and chemical stability in the majority of organic solvents. In combination with the availability of numerous modification routes to enhance the selectivity with respect to the target component, these features open prospects for very wide practical use of siloxane polymers. Their use is particularly promising in petroleum chemistry and organic synthesis for recovery from the reaction mixture and separation of reaction products, separation of homogeneous catalysts from reaction media, and fining processes (separation of sulfur-containing compounds) in oil refining. For example, Logemann et al. [147] demonstrated prospects for using a PDMS membrane for isolating hydroformylation products from reaction mixtures. Organophilic pervaporation of petroleum products on PDMS membranes also shows promise as a fining process [148, 149]. Modification of polysiloxanes can considerably expand the field of their successful use for separating various organic mixtures.

Zou et al. [150] suggested using a PDMS-based membrane with silicon dioxide and aerogel for corrosion protection of Li-ion batteries. This nonstandard use of siloxane membranes can become a new line in the studies on the development of oxygen-permeable membranes in designing metal–air batteries.

The use of siloxane membranes for nanofiltration of nonaqueous media also becomes popular [151–154]. In particular, there are studies aimed at using mixed matrix PDMS membranes for filtration of solutions of homogeneous catalysts [153, 154]. Introduction of nanofiller (zeolite, coal, silicalite) particles reduces the membrane swelling in high-solvency liquids (toluene, ethyl acetate) and allows high (up to 98%) catalyst retention to be reached [153].

Medicine is also an important application field of siloxane membranes owing to good biocompatibility of polysiloxanes. This field underwent active progress in the past decades. Shams et al. [155] reported the use of polyurethane/polysiloxane membranes filled with graphene oxide nanoplates as artificial skin. The bandages obtained showed good antimicrobial activity and cytocompatibility. The use of PDMS membranes for extracorporeal membrane oxygenation of blood has already become classical [156, 157]. PDMS shows good hemocompatibility, and the contact of the continuous membrane surface, in contrast to porous membranes, with blood reduces the probability of thrombus formation.

CONCLUSIONS

Polysiloxane polymers have found wide use as membrane materials for separating gases and liquids, primarily due to their high permeability, stability of transport properties, chemical durability, heat resistance, and good mechanical and film-forming properties. The unique flexibility of the polysiloxane chain and weak intra- and intermolecular interactions ensure high values of the segmental mobility and void volume of the polymer, and cross-linking ensures high mechanical properties of thin polysiloxane-based films and their stability in organic media. It should be noted that the transport and separation characteristics of polysiloxane polymers are stable in time.

Polysiloxanes allow selective recovery of bulky organic molecules from aqueous and gaseous media owing to increased dissolution selectivity in combination with low diffusion selectivity. Therefore, polysiloxane-based membranes are used for recovery of C3+ hydrocarbons from gas streams in petroleum chemistry (gas separation), treatment of air media to remove vapors of harmful organic substances (vapor separation), and recovery of valuable or contaminating organic compounds from aqueous media (pervaporation). Among polysiloxanes, polydimethylsiloxane (PDMS) is the most highly permeable; it has been studied in most detail and is the most widely used in gas separation and pervaporation. Membranes based on PDMS exhibit high throughput and high stability of transport properties, but their selectivity is insufficient for economically feasible separation of hydrocarbons.

Modification of polysiloxanes allows preparation of membranes with diverse transport properties for solving a wide range of separation problems. The one-step procedure for polysiloxane modification in the
The potential of using membranes of this type is high not only in traditional separation processes, but also in new fields that are being actively developed, in particular, in petroleum chemistry and organic synthesis in the context of modern trends toward power and resource saving and toward an increase in the share of large-tonnage fine chemical technology.

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CONFLICT OF INTEREST

The authors declare no conflict of interest requiring disclosure in this article.

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