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Macromolecular design of permselective membranes

Toshiki Aoki*

Faculty of Engineering and Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050,
Niigata 950-2181, Japan

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Abstract

This review article discusses mainly the relationship between the chemical structure of new macromolecules synthesized for permselective membranes and their permselectivity, published over the period of twelve years, from 1985 to June 1996. Therefore, this review deals with macromolecules having well-defined structures and with permselective membranes whose separation mechanisms depend on the chemical structures of the membrane polymer. This review describes oxygen permselective membranes which concentrate oxygen in air, ethanol permselective membranes which concentrate ethanol in dilute aqueous ethanol solution, and optical resolution membranes which concentrate one enantiomer in racemates. In addition, permselective membranes whose permeability or permselectivity are controlled by external stimulation are also described. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Permselective membranes; Oxygen permselective membranes; Ethanol permselective membranes; Optical resolution membranes; External stimulation of membranes; Chemical structure

Contents

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* Fax: + 81-25-262-6778.
E-mail address: toshaoki@eng.niigata-u.ac.jp (T. Aoki)

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1. Introduction

This review article discusses mainly the relationship between the chemical structure of new macromolecules synthesized for permselective membranes and their permselectivities, from literature published in the period 1985 to June 1996. This review deals with macromolecules having well-defined structures and with permselective membranes whose separation mechanisms depend on the chemical structures of the membrane polymer. This review describes oxygen permselective membranes which concentrate oxygen in air, ethanol permselective membranes which concentrate ethanol in dilute aqueous ethanol solution, and optical resolution membranes which concentrate one enantiomer in racemates. In addition, permselective membranes whose permeability or permselectivity are controlled by external stimulation are also described.

1.1. Permselective membrane

1.1.1. Development from porous membrane to non-porous membrane [1]

There are many kinds of permselective membranes which are classified by the size of permeating path

Table 1
The classification of perselective membranes

Membrane	Pore size (nm)	Separation mechanism	Membrane process
Porous membrane	ca. 5–500	Sieving	Microfiltration Ultrafiltration
		Poiseuille flow	
Microporous membrane	ca. 1–5	Knudsen flow	Reverse osmosis
Non-porous membrane	No pores	Solution–diffusion	Pervaporation Gas permeation

(hole) as shown in Table 1. Porous membranes separate substances based on sieving effect. In the membranes, smaller substances or molecules permeate more rapidly than larger substances or molecules and the separation mechanism is based only on the size of substances and on the permeating path (hole), and the chemical structures and their nature do not affect the permselectivity. Therefore, macromolecular design is not related to the development or improvement of porous membranes. For example, even in case of a porous membrane with small holes of <1 nm diameter, oxygen/nitrogen mixture cannot be separated because the permeation is governed by Knudsen flow. In this mechanism, since a permeability is inversely proportional to the square root of molecular weight of the permeant molecule, the permselectivity of oxygen/nitrogen is close to unity.

In order to overcome this limitation, new membranes were designed whose separation mechanism was based on a chemical interaction between a membrane material and a permeant. Such a membrane is particularly effective for separation of a liquid mixture. However, when the chemical interaction is too strong, the polymer membrane swells or dissolves in the permeant and the permselectivity disappears. Nakao et al. solved this problem by using a filling-polymerized membrane [2]. The membrane is composed of a porous substrate film which is inert to organic liquids and a filling polymer in the pore of the substrate which is soluble in a specific solvent. The difference in solubility of the filling polymer to permeant causes permselectivity and the substrate membrane restrains the swelling of the filling polymer. This membrane separated a benzene/cyclohexane mixture in pervaporation. These kinds of membranes whose mechanisms are based on the affinity between a permeant and a membrane polymer have no holes and are therefore called non-porous membranes or dense membranes. In the permeation through a non-porous membrane, permeating molecules first dissolve in the membrane surface and then diffuse in the membrane. In this case, permeability coefficient (P) is expressed by the product of solubility coefficient (S) and diffusion coefficient (D).

$$P = S \times D$$

For non-porous membranes, the chemical structure and molecular motion of the membrane polymer determine the separation performance. Therefore, it is important to design chemical structures which increase the difference in S and D between two molecules without decreasing S and D. Accurate molecular design is indispensable for a membrane with high performance.

1.1.2. High performance and limitation of carrier-containing membrane

Since D is dependent on the size of the permeating molecule, in order to separate two molecules

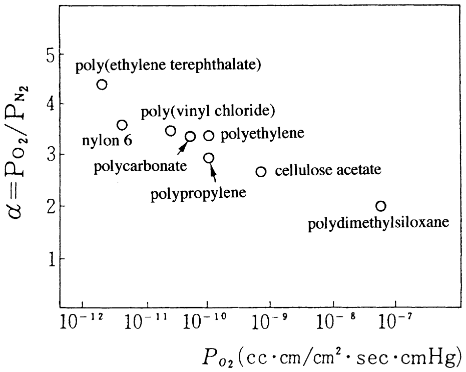


Fig. 1. A plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of commercially available polymers.

whose sizes are almost same, the difference in the S values of the two molecules is important. However, the difference of affinity for the membrane polymer between the permeating molecules is low in general: for example, S ratio between oxygen and nitrogen is about 2 at most. To overcome this limitation, molecular-recognizing carriers were incorporated into the membranes.

The membranes containing molecular-recognizing carriers, such as cobalt complexes for an oxygen permselective membrane and a chiral crown ether for an enantioselective permeation, were reported to show very high permselectivity. However, these high permselectivities were attained only in the case of liquid membranes containing the mobile carriers [3,4]. Therefore, the stability and durability of these membranes were low and they were not practical. Although, in order to enhance the stability, the carriers were incorporated into a solid membrane, the carriers were immobile and the content of the carrier in the membrane maintaining the membrane forming ability was low. For example, permeation through a solid membrane containing a cobalt porphyrin showed very high permselectivity but the selectivity was attained only when the feed pressure was low [5,6].

It was reported by Shinkai et al. that liquid membranes containing carriers which can respond to external stimulation such as light, redox, and pH showed additional performance such as active transport and switching transport for alkali metal ions [7,8]. Polymer/liquid crystalline (LC) composite membranes containing carriers in LC were reported as an optical resolution membrane [9], a membrane whose permeability was controlled by external stimulation [10], and oxygen permselective membrane [11]. In these membranes, carriers in LC were mobile because of low viscosity of the LC.

1.2. Oxygen permselective membrane

Oxygen permselective membranes produce oxygen-enriched air used for combustion (oxygen concentration: 30–40%) and medical care (oxygen concentration: 21%) from air. The requirements for this membrane are as follows:

1. High oxygen permeability.
2. High oxygen permselectivity.
3. High mechanical strength.
4. High stability.

Since oxygen and nitrogen molecules are almost the same in size (oxygen 0.38 nm, nitrogen 0.40 nm) and also because their properties are similar, polymers having a little difference between oxygen and nitrogen both in diffusivity (*D*) and solubility (*S*) are designed for these membranes. They have been partially applied for practical use but their permselectivities are low. Fig. 1 is a plot of oxygen permselectivity (oxygen separation factor, $\alpha = P_{O_2}/P_{N_2}$) versus logarithmic oxygen permeability coefficient (P_{O_2}) of commercially available polymers. In other polymers P_{O_2} increases with decrease in α, i.e. a trade-off relationship and an upper boundary line are present [12]. Polydimethylsiloxane (PDMS, **1**) shows the highest P_{O_2} but the lowest α.

In this review, the following units are used and are hereafter not repeated in the text:

- oxygen permeability coefficient, P_{O_2}: $\times 10^{-10}$ cm^3(STP) cm^{-2} s^{-1} cmHg^{-1} (= barrer);
- oxygen solubility coefficient, S_{O_2}: $\times 10^{-3}$ cm^3(STP) cm^{-3} cmHg^{-1};
- oxygen diffusion coefficient, D_{O_2}: $\times 10^{-6}$ cm^2 s^{-1};
- oxygen separation factor, $\alpha = P_{O_2}/P_{N_2}$.

Since these values do not depend on the form of the membrane such as membrane thickness and area and are intrinsic values, not for a given membrane but for a given polymer, they are suitable for discussion on the relationship between chemical structure and permeability. Our target values are $P_{O_2} > 100$ and $\alpha > 3.0$ at present.

1.3. Ethanol permselective membrane

To concentrate a dilute aqueous ethanol solution (5–10 wt%) obtained by fermentation of biomass, a membrane through which ethanol permeates more rapidly than water is expected. However, since the molecular radii of ethanol and water are 0.52 and 0.37, respectively, diffusion selectivity is water selective and therefore most of the polymeric membranes show water permselectivity and there are only a few ethanol permselective membranes. In order to attain ethanol permselectivity, membrane polymers that have higher affinity for ethanol than for water and small water-selective diffusion are designed.

Fluorine- and silicon-containing polymers are water repellent and therefore they are expected to give ethanol permselective membranes.

The author expresses permeation rates and ethanol permselectivity in the following units and does not repeat them in the article:

- permeation rate, *P*: $\times 10^{-3}$ g mm^{-2} h^{-1};
- Ethanol permselectivity, $\alpha^{\mathrm{EtOH}} = (Y_{\mathrm{EtOH}}/Y_{\mathrm{water}})/(X_{\mathrm{EtOH}}/X_{\mathrm{water}})$ where EtOH indicates ethanol, *X* the weight fraction of the feed and *Y* the weight fraction of the permeate;
- [EtOH]: ethanol concentration of the feed (wt%).

Since these values do not depend on the form of the membrane such as membrane thickness and area and are intrinsic values not for a given membrane but for a given polymer, they are suitable for discussion on the relationship between chemical structure and permeability. It should be noted that the strong interaction between membrane polymers and permeating liquid molecules affects the permeation behavior and therefore the values are not independent of the composition of the feed solution. This make the permeation behavior more complex than that in oxygen permeation. Our target values are $P > 2$ and $\alpha^{\mathrm{EtOH}} > 15$ at present.

1.4. Optical resolution membrane (enantioselectively permeable membrane)

Enantiomers are identical to each other not only in size but also in all physical properties except for optical rotation, but their biological activities are completely distinct. Optical resolution is a very important separation process and will become much more important in the field of medicine and agricultural chemicals, because the use of these chemicals in optically pure form is effective and safe. Conventional optical resolution methods have the common drawback that only a small amount of material can be treated in one operation. On the other hand, optical resolution by membrane permeation is very promising because a large amount of racemates can be handled in a single treatment.

Since the size of enantiomers are identical to each other, they cannot be separated through porous membranes based on sieving effect. This separation membrane must have chiral recognition sites for enantiomers.

The author expresses permeation rates, permeability coefficients and enantioselective permeability in the following units and does not repeat them hereafter in this article:

- permeation rate, P: $\times 10^{-7}$ g mm^{-2} h^{-1};
- permeability coefficient, P_c: $\times 10^{-10}$ m^2 h^{-1};
- enantioselective permeability: $=$ %ee of the permeate when a racemate is supplied.

Various separation processes were used: CP, concentration-driven permeation; PP, pressure-driven permeation; PV, pervaporation; and EV, evapomeation.

1.5. Membrane with permeability controlled by external stimulation

Permeation in response to external stimulation frequently occurs in biological membranes, but in case of synthetic membranes especially in case of solid membranes, such membranes are only a few. Some of the monomolecular membranes, bimolecular membranes and liquid membranes were reported to show permeation in response to external stimulation. However, since their structures were analogous to biological membranes, they were sensitive, in other words, unstable. Therefore, to attain stable permeation in response to external stimulation, new polymers whose structures are different from those of biological membranes must be designed.

2. Macromolecular design for oxygen permselective membrane

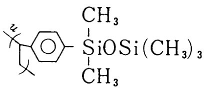
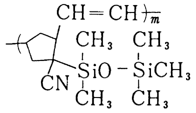
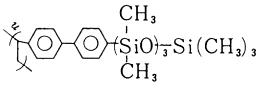
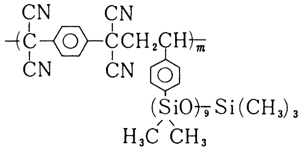
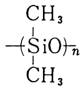
2.1. Relationship between a functional group in a macromolecule and oxygen permselectivity

Since the aim of this review is to discussion relationship between structure of a membrane polymer and its oxygen permselectivity, we describe mainly membranes consisting of a pure polymer while composite membranes and blend membranes are treated briefly. Polymers with relatively high P_{O_2} are described because permselective membrane should be highly permeable.

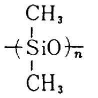
2.1.1. Silicon containing polymer

2.1.1.1. Siloxane (SiOSi bond) containing polymer. Polydimethylsiloxane (PDMS, **1**) is one of the most

Table 2
Effect of the backbone on oxygen permeation behavior in the siloxane comb-shaped polymers (the values in parentheses are those for the backbone polymers)

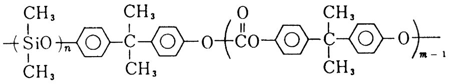
Polymer structure	PDMS (wt%)	T_g (°C)	P_{O_2} (× 10^{-9})	α
	59	36 (108)	4.0 (0.12)	3.0(5.5)
	59	88(140)	1.5(0.05)	3.5(6.3)
	62	−70	8.3	2.4
	71	−117	10.6	2.4
cf.  $-(\overset{CH_3}{\underset{CH_3}{Si}}O)_n-$	100	−123	48.9	2.0

important oxygen permselective membrane polymers because it shows the highest P_{O_2} (=350) amongst commercially available polymers. However, PDMS has the lowest α (=2.0) and possesses no membrane-forming ability.


$-(\overset{CH_3}{\underset{CH_3}{Si}}O)_n-$

: 1

When membrane-forming ability is imparted to PDMS maintaining high P_{O_2}, it can be applied for the production of oxygen-enriched air used for combustion. Ward III et al. synthesized PDMS-block-polycarbonate (PC) (**2**) from oligodimethylsiloxane with hydroxyphenyl groups at both ends, phosgene and bisphenol A, and found that it formed a thin membrane showing high permeability ($P_{O_2} = 200$ and $\alpha = 2.0$) [13]. Asakawa et al. prepared a crosslinked polymer (**3**) from polyvinylphenol (PVP) and PDMS with diethylaminosilyl groups at both ends and report good membrane-forming ability and high permeability ($P_{O_2} = 340$, $\alpha = 2.1$) [14]. By these chemical modifications of PDMS, membrane-forming ability was improved, but the P_{O_2} and α were not changed. The modified PDMSs **2** and **3** were applied to the production of air for combustion.



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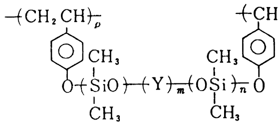


: 3

It is desirable that the second component such as PC and PVP mentioned above which was introduced in order to add membrane forming ability improves α while maintaining high P_{O_2}. Since in case of **2** and **3**, permeant gas molecules permeate only through the PDMS domain which was formed by micro-phase separation, the P_{O_2} and α were almost the same as those of PDMS. In order to enhance α while retaining high P_{O_2} by use of the second components, permeant gas molecules must permeate while being affected by both PDMS and the second component. On the basis of this consideration, Kawakami et al. synthesized new comb-shaped polymers (DMS content = 60–70 wt%) with short oligodimethylsiloxane chains (polymerization degree, $n = 2$–10) as grafts by homopolymerization of the corresponding macromonomer and measured their oxygen permeability (Table 2) [15–20]. In these comb-shaped polymers, the permeation properties of both components appeared and good performance ($P_{O_2} = 10$–100, $\alpha = 2.4$–4.4) was observed. This is because the two components mixed well in molecular size order and micro-phase separation did not occur. Therefore selection of the main chain structure is important. They selected second components having different nature from that of PDMS, i.e. high T_g, which is a rough measure of the membrane-forming ability, and high α. For example, polystyrene has $T_g = 108°C$ and $\alpha = 5.5$ and polynorbornene has $T_g = 140°C$ and $\alpha = 6.3$.

Kawakami et al. [20] and Nagase et al. [21,22] synthesized siloxane graft copolymers which have smaller number of longer siloxane graft chains (DMS content = 60–80 wt%) compared with comb-shaped polymers by copolymerization or polymer reaction. When the main chain was an alternating copolymer of styrene and tetracyanoquinodimethane, the polymerization degree of the grafts was 10, and DMS content was 71 wt%, P_{O_2} and α were 106 and 2.4, respectively. When the main chains were polysulfone (PSF) and polyimide (PI), the average polymerization degrees of the grafts were 7.2 and 11.1, and DMS contents were 65 and 60 wt%, P_{O_2} and α were 115 and 163, and 2.66 and 2.45, respectively.

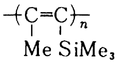
Siloxane block and alternating copolymers containing a second component were also reported. Nagase et al. measured the oxygen permeation behavior of a block copolymer of tetramethyl-*p*-silphenylenesiloxane and DMS [23]. When DMS content was 25 and 70 mol% (the average polymerization degree of PDMS in the block copolymer was 400), P_{O_2} and α were 14.1 and 248, and 2.77 and 2.12, respectively. Kiyotsukuri et al. reported that a polyamide (an alternating copolymer) from 1,3-bis(aminopropyl)disiloxane and aliphatic dicarboxylic acid showed values of 20.4 and 9.15 for P_{O_2} and 2.73 and 2.40 for α in 35.5 and 29.0 wt% of DMS content, respectively [24]. We synthesized a new polyazomethine containing an oligosiloxane and a pyridine ring alternatingly and found that its P_{O_2} was more than 100 [25]. P_{O_2} and α of a triblock copolymer of PDMS and poly(amino acid) having 54 mol% of DMS were 23 and 3, respectively [26].

2.1.1.2. Trimethylsilyl group containing polymer. Most of the polymers containing trimethylsilyl groups show relatively high α and P_{O_2} values. Kawakami et al. and Nagasaki et al. found that polystyrenes with trimethylsilyl, trimethylsilylmethyl and bis(trimethylsilyl)methyl group at the *para* position showed values 14, 14 and 45 for P_{O_2} and 3.4, 3.9 and 3.8 for α [27,28]. Poly(vinyltrimethylsilane) also showed good oxygen permeability ($\alpha = 4.4$ and $P_{O_2} = 44$). In these polymers, glass transition temperatures (T_g) and free volumes increased owing to the bulkiness of the trimethylsilyl group. Several trimethylsilyl containing polyacetylenes were also studied (see Section 2.1.2.2).

2.1.1.3. Alkoxysilyl group (SiOC bond) containing polymer. Compounds containing a SiOC bond are not suitable for membrane polymers because this bond is generally unstable to water and is easily hydrolyzed. However, the synthesis of this bond is very simple and if certain conditions are selected, hydrolysis can be avoided. We therefore use this bond actively. For example, *p*-diethoxymethylsilylstyrene gives a soluble high molecular weight polymer showing P_{O_2} 74.9 and α 2.99 [29]. In particular, our new polymers containing fluoroalkyloxysilyl groups were stable and showed high P_{O_2} and α [30] (see Section 2.1.2.3).

2.1.2. Poly(substituted acetylene)

2.1.2.1. General. Masuda et al. synthesized many soluble poly(substituted acetylene)s which showed high performance as oxygen permselective membranes [31,32]. Since when compared at a similar value of P_{O_2} they showed higher values than those of the other polymers, they were good polymers for oxygen permselective membranes (Fig. 2). In particular, poly(1-trimethylsilylpropyne) (PMSP, **4**) showed about 10 times higher P_{O_2} than PDMS which has the highest P_{O_2} amongst commercially available polymers.



$-\!\!\left(\underset{\mathrm{Me}}{\mathrm{C}}=\underset{\mathrm{SiMe_3}}{\mathrm{C}}\right)_{\!n}\!\!-$

: **4**

2.1.2.2. Silicon containing poly(substituted acetylene). PMSP shows the highest P_{O_2} (= 4000) (but the lowest α (= 1.6). This is because intermolecular space of this polymer is large owing to the stiffness of the main chain and trimethylsilyl groups with high mobility are located in a space between the main chains where oxygen molecules permeate [33–35]. Another reason is that this polymer has much higher content of microvoids than the other polymers in a glassy state. However, the P_{O_2} value of this membrane decreased with time and became 1/10 after 10 days at room temperature in vacuo. This decrease was caused by change or decrease of the intermolecular space during physical aging process or absorption of small molecular weight molecule [33–36]. When one of the methyl groups of PMSP was replaced by ethyl or propyl groups, P_{O_2} decreased significantly [32]. This also indicates the unique property of PMSP. Masuda et al. reported that poly(diphenylacetylene)s having a trimethylsilyl group at the *para* or *meta* position of the benzene ring showed the highest P_{O_2} (=2800) except for PMSP [37]. When one of the methyl groups of the polymer was replaced by a more bulky substituent, P_{O_2} decreased significantly similarly to the case of PMSP.

A graft copolymer consisting of PMSP backbone and PDMS grafts which were introduced by polymer reaction such as hydrosilation was reported to have a P_{O_2} of 130 and an α of 3.10 by Nagase et al. [38]. In

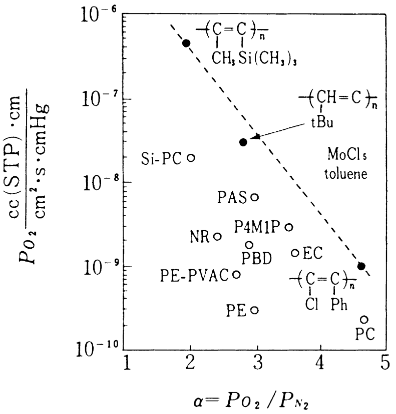
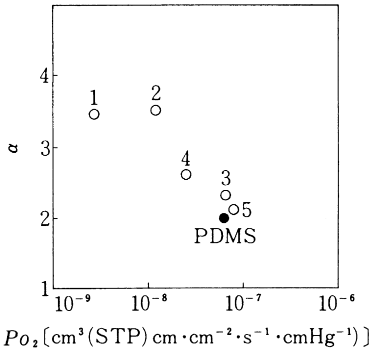


Fig. 2. A plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of poly(substituted acetylenes) (●) together with commercially available polymers (○). Si–PC, polydimethylsiloxane-block-polycarbonate (**2**); PAS, polyalkylsulfone; P4M1P, poly(4-methyl-1-pentene); NR, natural rubber; PBD, *cis*-1,4-polybutadiene; EC, ethyl cellulose; PE–PVAC, copoly(ethylene/vinyl acetate); PE, polyethylene; PC, polycarbonate (from Ref. [32]).

the case of less than 55 mol% of PDMS content, PDMS was packed into the intermolecular space of PMSP and the P_{O_2} decreased, while in the case of 55–60 mol%, PDMS continuous domain formed and P_{O_2} increased. When the PDMS content exceeded 60 mol%, the P_{O_2} and α values became similar to those of PDMS and the change in these values by aging, which had been observed in the case of PMSP, disappeared. P_{O_2} of poly(1-phenylpropyne) (PPP) having PDMS grafts increased with increasing the



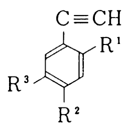
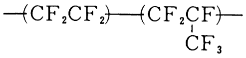
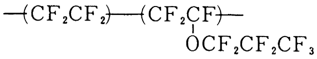
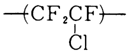
		R^1	R^2	R^3
	1 :	CF_3	H	H
	2 :	CF_3	H	CH_3
	3 :	CF_3	H	CF_3
	4 :	CF_3	CF_3	H
	5 :	CF_3	CF_3	CF_3

Fig. 3. A plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of poly(trifluoromethylphenylacetylenes) (●) together with polydimethylsiloxane (PDMS) (○) (from Ref. [41]). Solvent casting membranes from the homopolymer of monomers **1**–**5**.

Table 3
Oxygen permeation behavior of poly(tetrafluoroethylene) and its derivatives

Polymer structure	P_{O_2} (× 10^{-9})	α	S_{O_2}	S_{O_2}/S_{N_2}	Temperature (°C)
$-(CF_2CF_2)-$: (PTFE)	0.43	3.2	2.8	1.8	25
 $-(CF_2CF_2)-(CF_2CF(CF_3))-$	0.49	3.1	2.7	1.6	25
 $-(CF_2CF_2)-(CF_2CF(OCF_2CF_2CF_3))-$	0.42	3.5	–	–	22, 23
 $-(CF_2CF(Cl))-$	0.004	–	–	–	40
$-(CF_2CF_2)-(CH_2CH_2)-$	0.053	2.9	–	–	23
cf. $-(CH_2CH_2)-$ (HDPE)	0.039	2.7	0.24	1.2	25

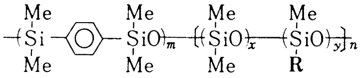
PDMS content (when 55 mol% $P_{O_2} = 80$, $\alpha = 2.9$) and with the PDMS content of more than 60 mol% the values were close to those of PDMS.

We synthesized phenylacetylenes having one or two trimethylsilyl group in the phenyl group and the monomers polymerized to yield a soluble polymer showing good membrane-forming ability and high P_{O_2} and α values [39]. In particular, poly[2,4–bis(trimethylsilyl)phenylacetylene] had a good performance ($P_{O_2} = 473$, $\alpha = 2.65$). The number and position of the trimethylsilyl substituent affected P_{O_2} and α values significantly. The changes of P_{O_2} of these polymers upon aging were small. In addition, we found that other polyphenylacetylenes with oligosiloxanes showed a good membrane-forming ability and higher P_{O_2} values than the ones containing a trimethylsilyl substituent [40]. For example, P_{O_2} and α

Table 4
Oxygen permeation behavior of poly(tetrafluoroethylene) and its derivatives having ionic groups

Polymer	P_{O_2} (× 10^{-9})	α	S_{O_2}	S_{O_2}/S_{N_2}	Temperature (°C)
Nafion® 117	0.108	4.15	2.39	1.59	35
Nafion® 125	0.14	2.2	1.6	2.2	30
Perfluorocarboxylate					
H^+ form	0.097	4.04	–	–	25
Ag^+ form	0.06	4.3	2.1	1.3	25
NEt_4^+ form	0.1	4.0	2.5	1.9	25
Nafion® 125 + Ag	0.16	11	3.0	6.6	25

Table 5
Effect of introduction of fluorine-containing groups of PDMS–PMPS block copolymers on oxygen permeation behavior

R in 	PMPS (mol%)	P_{O_2} ($\times 10^{-9}$)	α
$-CH_3$	50	5.2	2.30
$-CH_2CH_2CF_3$	50	6.5	2.41
$-CH_2CH_2C_8F_{17}$	54	5.3	2.42
$-CH_2CH_2C_6F_5$	50	7.3	2.44
$-CH_3$	22	32.3	2.04
$-CH_2CH_2CF_3$	25	19.4	2.28
$-CH_2CH_2C_8F_{17}$	28	14.7	2.35
$-CH_2CH_2CH_2CH_2OC_6F_5$	30	19.9	2.25
$-CH_2CH_2CH_2OCF(CF_3)_2$	25	27.6	2.34

values of poly(hexamethyltrisiloxanylphenylacetylene) and poly(octamethyltetrasiloxanylphenylacetylene) were 397 and 2.20, and 494 and 2.20, respectively.

2.1.2.3. Fluorine containing poly(substituted acetylene). Phenylacetylenes having one to three trifluoromethyl groups were synthesized and polymerized and the P_{O_2} and α of these polymer membranes were measured (Fig. 3) [41]. With increasing the number of the substituents, P_{O_2} increased and α decreased. In the case of one trifluoromethyl group, D_{O_2} increased owing to its bulkiness and in the case of two or three trifluoromethyl groups S_{O_2} increased owing to its affinity for oxygen. When trifluoromethyl group was changed to perfluoropropyl or perfluorohexyl group, P_{O_2} decreased.

p-(1H,1H,2H,2H-Perfluorodecyloxydimethylsilyl)phenylacetylene and *p*-(1H,1H,2H,2H-perfluorohexyloxydimethylsilyl)phenylacetylene were synthesized and copolymerized with *p*-trimethylsilylphenylacetylene [30]. The resulting copolymers were fabricated to form tough membranes showing high P_{O_2} (=394, 351) and α (=2.89, 3.04), respectively. The values were in the top level and very close to those of the upper boundary line [12] in an α–P_{O_2} plot of data in the literature.

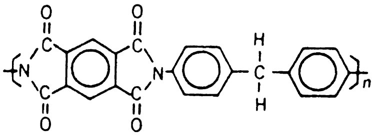
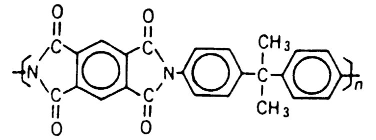
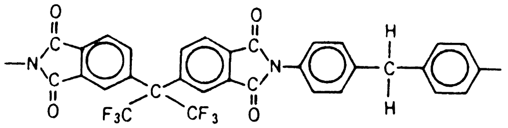
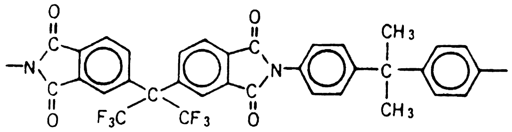
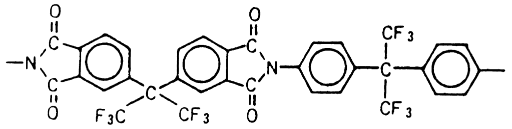
A plasma-polymerization membrane prepared from trimethylsilylpropyne and perfluorohexane showed higher α but the P_{O_2} decreased to 1/100 of the value of PMSP ($P_{O_2} = 20$, $\alpha = 2.5$) [42].

2.1.3. Fluorine containing polymers

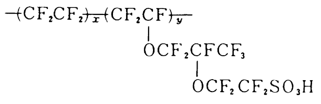
2.1.3.1. Polymers containing perfluoroalkylene group in the main chain. Table 3 summarizes oxygen permeation behavior of poly(tetrafluoroethylene) and its derivatives [43]. These P_{O_2} values are very low. Since oxygen permeates through the amorphous and not through the crystalline region, the low P_{O_2} value is caused by the high crystallinity.

P_{O_2} values of poly(tetrafluoroethylene)s with ionic groups such as Nafion (**5**) were smaller than those of poly(tetrafluoroethylene) as shown in Table 4 [44,45]. These polymer membranes have two regions where oxygen can permeate: the amorphous region of the perfluorocarbon and the cluster of the ionic

Table 6
Effect of introduction of trifluoromethyl groups of polyimides on oxygen permeation behavior (35°C)

	Polymer structure	P_{O_2} (× 10^{-9})	α	D_{O_2}	S_{O_2}
1		0.098	4.9	–	–
2		0.710	4.7	–	–
3		0.460	5.7	0.0426	10.8
4		0.753	5.6	0.0636	11.8
5		1.63	4.7	0.125	13.0

groups. Judging from the P_{O_2} value, most of the oxygen molecules permeated the amorphous region and the cluster region functioned as a crosslinking point. In order to enhance the α value, the cluster region should be used as permeating route. For example, in a Nafion–silver micro-composite membrane, α increased to 11 owing to the channel formed in the cluster region (see Table 4) [46].



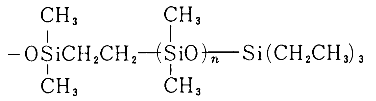
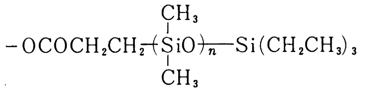
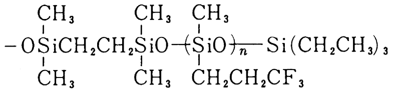
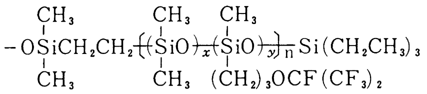
$$\begin{array}{l} -\!(CF_2CF_2)_x\!-\!(CF_2CF)_y\!- \\ \qquad\qquad\quad | \\ \qquad\qquad OCF_2CFCF_3 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad OCF_2CF_2SO_3H \end{array}$$

: 5

In order to obtain a new poly(tetrafluoroethylene) derivative, we synthesized a trifluorovinyl monomer and tried to apply it to an oxygen permselective membrane [47].

2.1.3.2. Polymers containing perfluoroalkyl group in the side chains. In order to improve α of polymers

Table 7
Oxygen permeation behavior of fluorine-containing PDMS-ethyl cellulose graft copolymers

Side chain structure	n	PDMS (mol%)	P_{O_2} ($\times 10^{-9}$)	α
 $-O\overset{CH_3}{\underset{CH_3}{Si}}CH_2CH_2-(\overset{CH_3}{\underset{CH_3}{Si}}O)_n-Si(CH_2CH_3)_3$	40	80	10.1	3.0
 $-OCOCH_2CH_2(\overset{CH_3}{\underset{CH_3}{Si}}O)_n-Si(CH_2CH_3)_3$	21	74	8.0	3.2
 $-O\overset{CH_3}{\underset{CH_3}{Si}}CH_2CH_2\overset{CH_3}{\underset{CH_3}{Si}}O-(\overset{CH_3}{\underset{CH_2CH_2CF_3}{Si}}O)_n-Si(CH_2CH_3)_3$	28	65	19	3.0
 $-O\overset{CH_3}{\underset{CH_3}{Si}}CH_2CH_2\{(\overset{CH_3}{\underset{CH_3}{Si}}O)_x(\overset{CH_3}{\underset{(CH_2)_3OCF(CF_3)_2}{Si}}O)_3\}_n Si(CH_2CH_3)_3$	21	40	4.4	3.9
$-OH$ (ethyl cellulose)	–	0	2.65	3.15

having high P_{O_2} but low α, introducing of fluorine-containing groups has been reported. The effect was not always high, but characteristic effects were observed.

PDMS has high P_{O_2} (= 350) and low α (= 2.0) as described above. Some attempts to enhance the α value while maintaining high P_{O_2} were made by introducing fluorine-containing groups. When replacing CH_3– by $CF_3CH_2CH_2$–, P_{O_2} decreased but α did not change [48]. This drop may be caused by the decrease in D_{O_2} by the bulkiness. No enhancement of α may be because the low content of fluorine-containing groups cannot increase S_{O_2}. A similar example was reported in poly(*p*-pentamethyldisiloxanylstyrene) [49].

However, by changing the mode of substitution of fluorine-containing groups, we were able to enhance both P_{O_2} and α simultaneously. For example, when trifluoropropyl groups or heptadecafluorodecyl groups was introduced to the side chains of the block copolymer of poly(tetramethyl-*p*-silphenylenesiloxane) (PMPS) and PDMS, P_{O_2} and α simultaneously increased as shown in Table 5 [50]. We also found simultaneous increase in the case of change of CH_3– to $CF_3(CF_2)_nCH_2CH_2O$– in a trimethylsilyl group of *p*-substituted polystyrene [51] and polyphenylacetylene (**6**) [30].

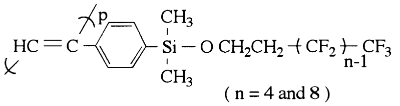
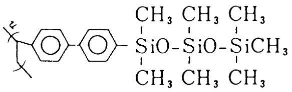
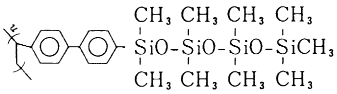
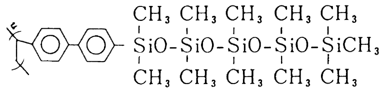
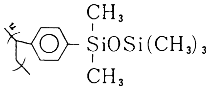
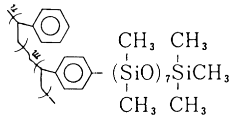

(n = 4 and 8)
:6

Table 8
Effect of the side chains on oxygen permeation behavior in the siloxane comb-shaped polymers

Polymer structure	PDMS (wt%)	T_g (°C)	P_{O_2} (× 10^{-9})	α
	55	−40	5.2	2.5
	62	−70	8.3	2.4
	67	−80	10.9	2.3
	59	36	4.0	3.0
	43	–	2.0	2.8

Oxygen permeability of fluorine-containing polyimides were also investigated [52–54]. As shown in Table 6, by replacing $-CH_3$ with $-CF_3$, P_{O_2} (and D_{O_2}) increased and α decreased (Nos. 4 and 5). This change resulted from enlargement of the space between the macromolecules by the bulky group. When a fluorine-containing group was introduced in other modes, both P_{O_2} and α increased (Nos. 1–3 and Nos. 2–4 in Table 6).

In ethylcellulose with PDMS grafts, which shows good P_{O_2} (=101) and α (=3.0), the methyl groups were substituted by several fluorine-containing groups. The substitution resulted in a good improvement of P_{O_2} and α (Table 7) [55].

In case of polyvinylacetal also, introduction of fluorine-containing groups brought about enhancement of P_{O_2} and decrease of α ($P_{O_2} = 11.9$, $\alpha = 4.4$) [56].

Although there have been many reports on the introduction of one or two CF_3 groups, P_{O_2} values increased while α values decreased and enhancement of α by oxygen affinity of fluorine-containing compounds was not observed in these cases. This may be because CF_3 group worked as a bulky group. In order to enhance α while maintaining high P_{O_2}, it is necessary that higher content of fluorine-containing compounds are incorporated without crystallization.

2.1.3.3. Fluorine containing plasma membrane. Polytetrafluoroethylene and its derivatives have two

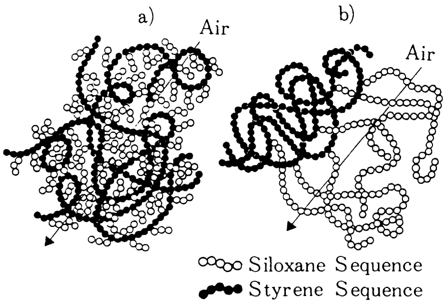


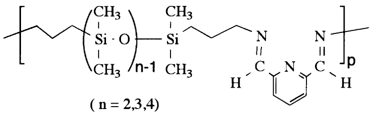
Fig. 4. Imaginative air permeation scheme through (a) short-branched (non-phase-separated) and (b) long-branched polymer membranes (from Ref. [16]).

defects, low P_{O_2} and poor membrane-forming ability, owing to close packing or high crystallinity of the perfluoroalkyl groups. These defects can be removed by using plasma polymerization of perfluorinated compounds.

When perfluorobenzene (PFB) was used as a monomer, good membrane having P_{O_2} of 200 and α of 3.5 was obtained [57]. When using a mixture of PFB and CF_4, P_{O_2} decreased but α increased significantly ($P_{O_2} = 11.8$, $\alpha = 7.2$). Contents of perfluoroalkyl chains in this membrane was enhanced by adding CF_4 [58]. In case of perfluoroalkyl acrylates, monomers having higher contents of fluorine tended to show higher values of α (3.8 for octafluoropentyl acrylate) [59]. A plasma polymerization membrane from a silicon containing compound and fluoromethane showed α higher than that from a silicon containing compound alone ($P_{O_2} = 15$, $\alpha = 3.9$). The significance of C–F bonds was suggested [60].

2.1.4. Others

Some of the pyridine ring containing polymers were reported to show relatively high α and P_{O_2}. Poly(4-vinylpyridine) shows a P_{O_2} of 10 and an α of 3.9. A plasma polymerization membrane from 4-vinylpyridine or 2-vinylpyridine has a high α lying in the range 6–15 [61]. We also synthesized pyridine-containing polyamides, polyazomethines (**7**) and poly(azomethine-amide)s and measured their oxygen permeability [25,62].



:7

In polymers having P_{O_2} of about 10, poly(4-methyl-1-pentene) ($P_{O_2} = 32.3$, $\alpha = 4.1$) and poly(2,6-dimethylphenylene oxide) ($P_{O_2} = 15.8$, $\alpha = 4.2$) have higher α values than other commercially available polymers. Polystyrene ($P_{O_2} = 2.0$, $\alpha = 6.4$) and poly(vinyl acetate) ($P_{O_2} = 0.2$, $\alpha = 7.0$) also show higher α than other polymers having a similar P_{O_2}. Poly(*t*-butylstyrene) was reported to show excellent permselectivity ($P_{O_2} = 10$, $\alpha = 7.0$) [63].

Phosphazene polymer shows a P_{O_2} value of more than 100. The permeability was varied by changing the substituents ($P_{O_2} = 3.1$–128, $\alpha = 2.3$–3.6) [64]. Silicon-containing fumarate copolymer also showed a P_{O_2} value greater than 100 [65].

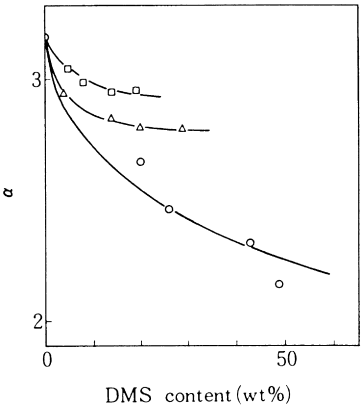


Fig. 5. Plots of oxygen permselectivity (α) versus dimethylsiloxane (DMS) content of PMPS–PDMS block copolymer (**9**). ○, $y = 100$; △, $y = 40$; □, $y = 20$ (from Ref. [66]).

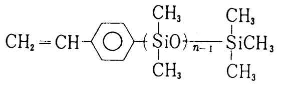
2.2. Relationship between architecture of a macromolecule and oxygen permselectivity

In Section 2.1, the relationship between the chemical structure (functional group) of a macromolecule and its oxygen permselectivity was described. Oxygen permselectivity is largely affected by the architecture of the macromolecule even if they have the same compositions. In this section, oxygen permselectivities of polymers having different architectures with the same composition are discussed.

2.2.1. Comb-shaped polymers and graft copolymers

Both a comb-shaped polymer and a graft polymer are composed of a backbone and grafts and there is no distinct boundary line between the two. In this review, a polymer with a great number of short grafts is defined as a comb-shaped polymer and a polymer with a small number of long grafts is defined as a graft polymer.

Kawakami et al. synthesized a comb-shaped polymer and a graft polymer consisting of a polystyrene backbone and PDMS grafts by homo- or copolymerization of the corresponding macromonomer (**8**) (Table 8) [15–19]. A comb-shaped polymer showed a higher α and better membrane-forming ability than a graft polymer having a similar siloxane content. Since in a comb-shaped polymer the main chain and the grafts mixed more homogeneously and microphase separation did not occur, this polymer had both advantages of the main chain and the grafts, i.e. high α and good membrane-forming ability. On the other hand, in a graft polymer where microphase separation occurred since air permeates through only PDMS region, α was low (Fig. 4). Such comb-shaped polymers, composed of a rigid main chain and flexible side chains, are suitable as a good oxygen permselective membrane. In this polymer, the main chain plays a role in permselectivity and membrane-forming ability and the short side chains play a role in permeability.



$CH_2{=}CH{-}C_6H_4{-}(Si(CH_3)_2O)_{n-1}{-}Si(CH_3)_2CH_3$

: 8

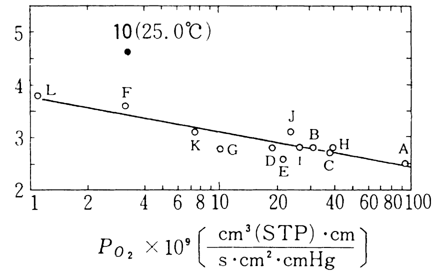


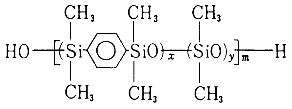
Fig. 6. Plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of poly(silsesquioxane) (**10**, ●) together with siloxane-containing polymers (A–L, ○) at 35°C (from Ref. [68]).

We synthesized poly(*p*-oligosiloxanylphenylacetylene)s as new comb-shaped polymers and measured their oxygen permselectivities [40]. These polymers showed better membrane-forming ability and much better oxygen permselectivities than the corresponding polystyrenes mentioned above. We also studied the corresponding graft copolymers.

2.2.2. Alternating and block copolymers

In case of a linear polymer, the relationship between an alternating and a block copolymer corresponds to the relationship between a comb-shaped and a graft polymer.

Block copolymers of poly(tetramethyl-*p*-silphenylenesiloxane) (PMPS) and PDMS having a different length were examined (**9**) [66]. With decreasing length of PDMS the crystallinity of PMPS decreased and P_{O_2} increased (when compared at the same PDMS content) (Fig. 5). When increasing PDMS content, the degree of decrease in the α of polymer containing short PDMS chains was smaller than that containing long PDMS chains. This may be because shorter PDMS chains were able to mix with PMPS chains better and permeating molecules were affected by PMPS more effectively (PDMS = 19 wt%, $P_{O_2} = 230$, $\alpha = 3.0$). Therefore, an alternating copolymer was expected to be a good oxygen permselective membrane.



$$HO-[(Si(CH_3)_2-C_6H_4-Si(CH_3)_2O)_x-(Si(CH_3)_2O)_y]_m-H$$

: **9**

We synthesized an alternating copolymer of aromatic rings and an oligosiloxane and found that the higher the homogeneity of two components, the higher the α was for a similar PDMS content [67].

2.2.3. Ladder-like and linear polymers

Ladder-like polymers are interesting in view of possibility of a molecular sieving membrane. Stern et al. reported polyphenylsilsesquioxane (**10**) which showed higher α than other siloxane containing polymers (Fig. 6) [68]. We tried to prepare a ladder-like polymer from *p*-alkoxysilylphenylacetylene and found the α was enhanced by the formation of a ladder-like structure [69].

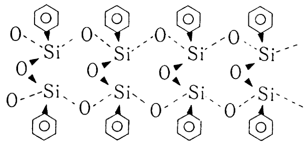


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Fig. 7 summarizes the effect of the chemical structure on the oxygen permeation behavior. One can understand the good performance of poly(substituted acetylene)s and the good effects of introducing fluorine-containing groups.

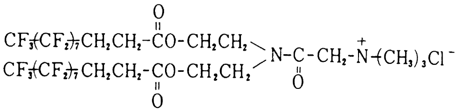
2.3. Composite membrane containing a compound having oxygen affinity

Although it is difficult to discuss the relationship between permselectivity and macromolecular structure in the case of composite membranes, they are important in view of their high performance. Therefore, in this section, we describe them briefly.

2.3.1. Addition of a compound having oxygen affinity (blend membrane)

2.3.1.1. Fluorine containing compounds. Kajiyama et al. reported that a composite membrane consisting of perfluorotributylamine (PFTA) with high oxygen affinity, *N*-(4-ethoxybenzylidene)-4′-butylaniline (EBBA) having the ability to form a liquid crystal, and poly(vinylchloride) showed good performance ($P_{O_2} = 10.2$, $\alpha = 5.10$) [70]. When PFTA was absent, both α and P_{O_2} were lower ($P_{O_2} = 5.75$, $\alpha = 2.95$). A significant effect of the fluorine compound was observed.

Kunitake et al. prepared a blend membrane consisting of polyvinylalcohol (PVA) and a fluorine-containing amphiphilic compound (**11**) [71]. The P_{O_2} and α of the membrane were about 100 times and 1.8 times higher than those of PVA, respectively ($P_{O_2} = 220$, $\alpha = 2.3$ at 100°C). In the case of a corresponding amphiphilic compound containing no fluorine atoms, α was almost the same as that of PVA itself and P_{O_2} was only 3 times higher (30°C).



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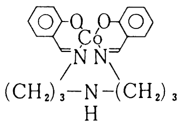
Kawakami et al. improved α of a block copolymer of PDMS and polycarbonate by adding a small amount of fluorine-containing polymers while maintaining high P_{O_2} ($P_{O_2} = 26.0$–27.4, $\alpha = 2.30$–2.63) [72].

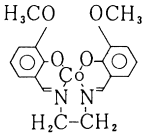
Chen et al. reported very high performance of a PMSP-based blend membrane containing poly(hexafluorobutyl methacrylate) ($P_{O_2} = 1390$, $\alpha = 5.4$) [73].

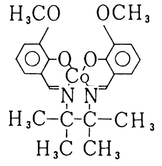
2.3.1.2. Cobalt complexes. Nishide et al. reported very high oxygen permselective polymeric membranes containing cobalt porphyrin or cobalt salen complex with high selectivity for oxygen. High α value was observed in the case of a low feed pressure [74–79].

Table 9
Oxygen permselective liquid membranes containing cobalt complex

Complex	P_{O_2} ($\times 10^{-9}$)	α
Co(SalPr)[a]	150	30
Co(3-MeOSalen)[b]	78	11
Co(3-MeOSaltmen)[c]	100	18
cf. Silicone rubber	50	2

[a]


[b]


[c]


Four types of polyazomethines containing repeated pairs of a tridentate ligand and an oligodimethylsiloxane ($n = 2, 3, 4$ or 16) in the backbone were synthesized and complexed with a cobalt ion by us [80,81]. The resulting polymer complex membranes showed very good oxygen permselectivity ($P_{O_2} = 291$, $\alpha = 3.4$) at 1 atm pressure difference which were very close to those of an upper boundary line [12] in an α–P_{O_2} plot of reported data in the literature. The complexes were thought to function as an oxygen carrier [80,81].

Lonsdale et al. developed a very high oxygen permselective liquid membrane containing cobalt salen complex as shown in Table 9. The life time was more than three months in spite of it being a liquid membrane [3,82].

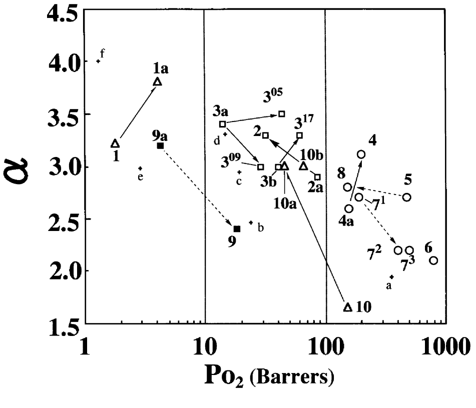
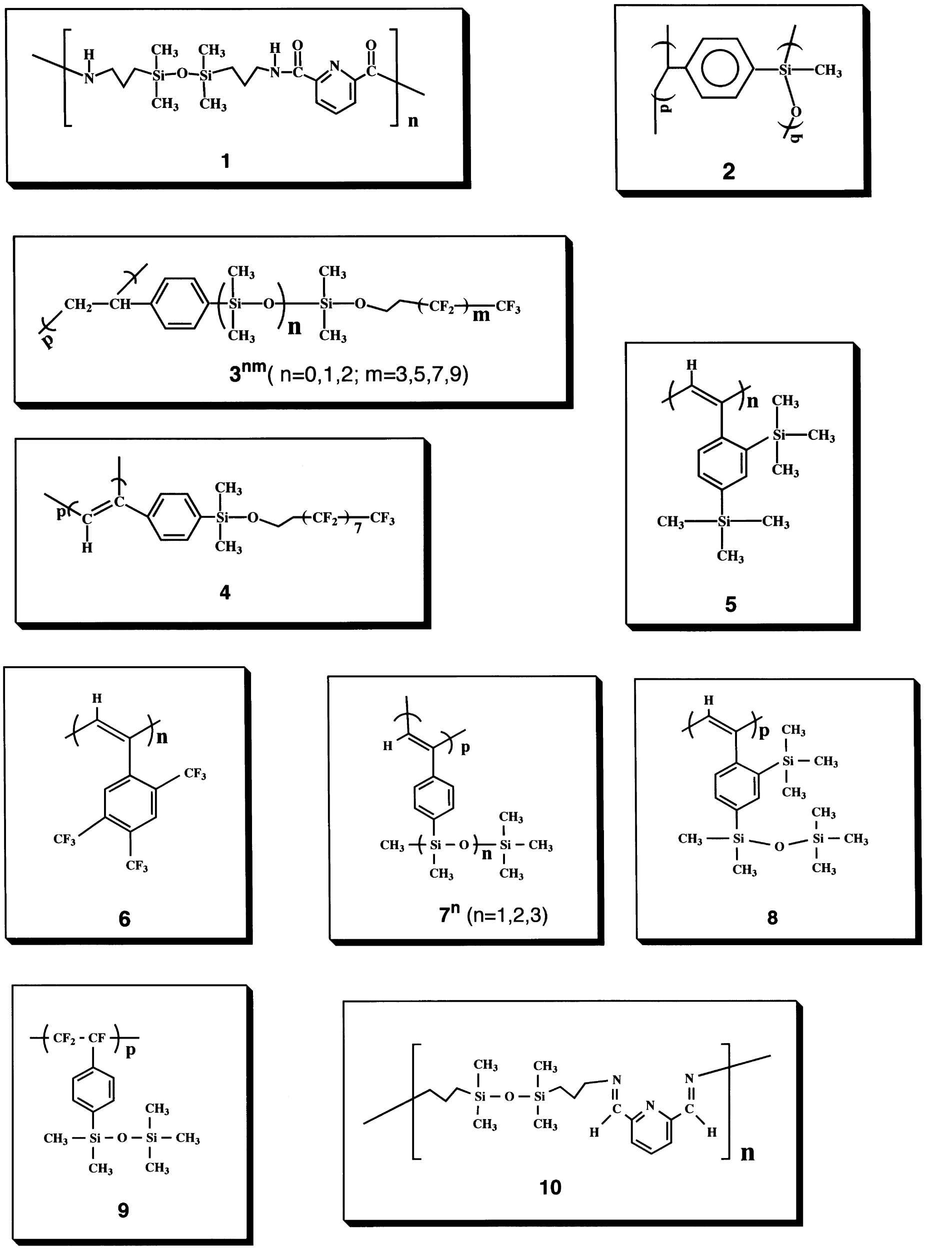


Fig. 7. A plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of various polymers containing short oligosiloxane chains. **1**–**10**: polymers containing short ologosiloxane chains (see equations). ○ ●, Poly(substituted phenylacetylene); △, polycondensation polymer; □ ■,: poly(substituted styrene); ●, ■, fluorine-containing polymer; a–f: commercially available polymers. ⟶ , effect of introduction of fluorine-containing substituents; ----▸, effect of introduction or extension of ologosiloxane chains; ⟶ , effect of addition of cobalt salts. **1a**, **1** + $CoCl_2$; **2a**, precursor of **2**, poly(*p*-diethoxymethylsilylstyrene); **3a**, poly(*p*-trimethylsilylstyrene); **3b**, poly(*p*-pentamethyldisiloxanylstyrene); **4a**, poly(*p*-trimethylsilyphenylacetylene); **9a**, poly (tetrafluoroethylene); **10a**, **10** + $CoCl_2$; **10b**, polycondensation copolymer of **1** and **10**; a, polydimethylsiloxane; b, natural rubber; c, poly(cis-1,4-butadiene); d, ethyl cellulose; e, low density polyethylene; f, butyl rubber.



1

2

3^{nm}(n=0,1,2; m=3,5,7,9)

4

5

6

7^{n} (n=1,2,3)

8

9

10

Fig. 7. (*continued*)

2.3.2. Surface modification by a compound having oxygen affinity

We improved both the α and P_{O_2} of PDMS or PMSP by adding a small amount (1.0 wt%) of fluorine-containing poly(arylacetylene)s as shown in Fig. 8 ($P_{O_2} = 730$ and 5200, $\alpha = 2.2$ and 1.8, respectively) [83]. This was caused by the selective dissolution of oxygen to the fluorine-containing polymer accumulated at the surface of the blend membrane.

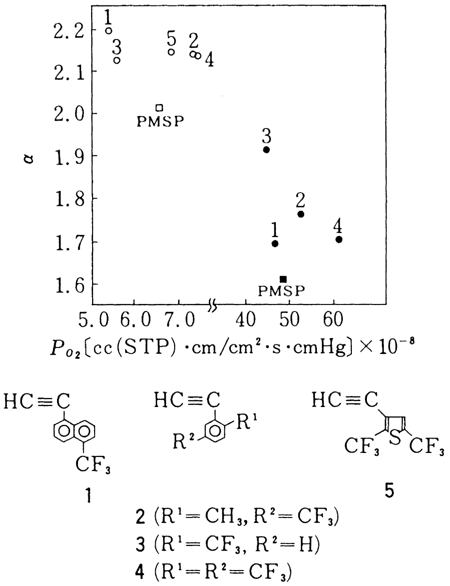


Fig. 8. Plot of oxygen permselectivity (α) versus oxygen permeability coefficient (P_{O_2}) of PDMS (○) and PMSP (●) containing a polymer of trifluoromethylarylacetylenes (**1**–**5**). Solvent casting membranes of PDMS and PMSP containing 1.0 wt% of homopolymer of **1**–**5** (from Ref. [83]).

A PMSP membrane whose surface was modified with a fluorine compound formed by plasma polymerization of perfluoroalkylethyl alcohol showed a value of 1000 for P_{O_2} and 3.6 for α [84].

Langsam et al. fluorinated the surface of a PMSP membrane by using F_2 and found a large enhancement of α while maintaining a high P_{O_2} ($P_{O_2} = 1960$, $\alpha = 4.75$) [85,86].

3. Macromolecular design for ethanol permselective membrane

3.1. Relationship between functional group in a macromolecule and ethanol permselectivity

3.1.1. Silicon-containing polymers

Most of the polymeric membranes show water permselectivity based on water selective diffusivity and therefore ethanol permselective membranes are only a few and their α^{EtOH} values are low. For example, the α^{EtOH} values of PMSP and PDMS are 10.3 ([EtOH] = 6–7 wt%) and 7.6, respectively.

Graft copolymers consisting of a PMSP backbone with PDMS grafts and of a PPP backbone with PDMS grafts, mentioned in Section 2.1.2.2, showed high α^{EtOH} of 28 and 40, respectively. When the main chains were PSF and PI (see Section 2.1.1), α^{EtOH} values were 7.19 and 5.14, respectively [21,22,87,88]. When a rigid main chain with no affinity for ethanol was used for a PDMS graft copolymer, they showed high ethanol selectivity. This is because swelling of the membrane by ethanol was avoided by the rigid main chain.

Although a polyphenylacetylene is water-selective in PV, trimethylsilyl substituted polyphenylacetylenes showed an ethanol permselectivity ($\alpha^{\mathrm{EtOH}} = 2.1$–$2.4$, $P = 0.19$–5.4) [39].

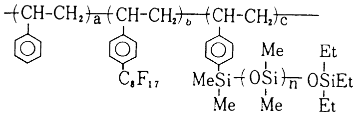
Adding hydrophobic zeolite to PDMS enhanced the α^{EtOH} from 7.6 to 16.5. Since an ethanol molecule can permeate through the pores of the zeolite but a water molecule cannot, water permeability decreased and ethanol selectivity increased [89].

A plasma polymerized membrane from a silicon-containing monomer was reported to be ethanol permselective having a α^{EtOH} of 16.9 [90].

3.1.2. Fluorine-containing polymers

A graft copolymer having PDMS and heptadecafluorooctyl group as grafts were synthesized (**12**). The α increased owing to high water repellency at the membrane surface ($[\mathrm{EtOH}] = 7$ wt%, $\alpha^{\mathrm{EtOH}} = 25.4$, $P = 0.27$) [91].

P and α^{EtOH} of copolymers of tetrafluoroethylene with alkylvinyl ether (**13**, **14**) or trifluorovinyl ether (**15**) were 0.5 and 7.1 ($[\mathrm{EtOH}] = 15$ wt%), and 0.8 and 7.2 ($[\mathrm{EtOH}] = 9$ wt%), respectively [92].



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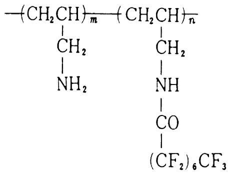
$CH_2=CH-O-C_{18}H_{37}$: 13

$CH_2=CH-O-CH_2-CH(C_2H_5)-C_4H_9$: 14

$CF_2=CF-O-CF_2-CF_2-C(CF_3)_2-OH$: 15

A fluorinated polymer (**16**) prepared by modification of water-soluble polyallylamine showed ethanol selectivity ($[\mathrm{EtOH}] = 5$ wt%, $\alpha^{\mathrm{EtOH}} = 3.5$) [93]. The higher the hydrophobicity of the surface was, the higher was the α^{EtOH}.

By introducing perfluoroalkyloxy groups to a poly(trimethylsilylphenylacetylene), α^{EtOH} and P were increased ($\alpha^{\mathrm{EtOH}} = 2.0$–$3.2$) [30].



$$-(\underset{\substack{|\\ CH_2\\ |\\ NH_2}}{CH_2CH})_m-(\underset{\substack{|\\ CH_2\\ |\\ NH\\ |\\ CO\\ |\\ (CF_2)_6CF_3}}{CH_2CH})_n-$$

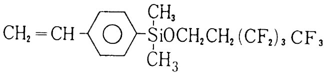
: 16

A composite membrane of PDMS and a graft copolymer of nonafluorohexyl acrylate or heptadecafluorodecyl acrylate with styrene showed a high α^{EtOH} ($[\mathrm{EtOH}] = 8$ wt%, $\alpha^{\mathrm{EtOH}} = 24.7$ and 45.9, $P =$ 1.62 and 0.60, respectively) [94].

3.2. Membrane surface-modified by fluorine-containing polymer

We enhanced the α_{EtOH} of PDMS by modifying its surface with fluorine-containing polymers without drop in P [95–97]. In particular, PDMS membranes whose surface was modified with a small amount of poly(*p*-perfluoroalkyloxydimethylsilylstyrene) (**17**) had good ethanol permselectivities

([EtOH] = 2.5 wt%, $\alpha^{EtOH} = 22.3$, $P = 206$) [95]. In these membranes, since only the surface was modified by the fluorine-containing polymer and the bulk was almost pure PDMS, α^{EtOH} increased while maintaining high permeability. When adding perfluoroalkyltriethoxysilane also, α^{EtOH} and P increased simultaneously. Moreover, by hydrolysis-condensation the α^{EtOH} was increased further [97].



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4. Macromolecular design for optical resolution membrane (enantioselectively permeable membrane)

4.1. Shortcomings of conventional optical resolution methods

Conventional optical resolution methods, including preferential crystallization, chemical modification by an optical resolution agent and high-performance liquid chromatography (HPLC) with a chiral stationary phase, have the common drawback that only a small amount of material can be treated in one operation. On the other hand, optical resolution by membrane permeation is very promising because a large amount of racemates can be handled in a single treatment.

4.2. Conventional approach to design an optical resolution membrane

Optical resolution membranes reported so far [4,98–103] are divided into two groups. One is membranes containing enantiomer-recognizing carriers [4,98,99] and the other is prepared from a polymer of a chiral stationary phase in HPLC [100–103]. Liquid membranes containing enantiomer-recognizing carriers such as a chiral crown ether showed highly enantioselective permeability [4] but low durability because loss of the liquid and carriers could not be avoided. In case of solid membranes containing enantiomer-recognizing carriers, their durability becomes high but the enantioselectivity is observed only at an initial period owing to saturation of the carriers by permeants. The saturation may occur because the carriers are not mobile but fixed, and moreover the content of the carriers in a membrane together with self-supporting membrane-forming ability is limited. For example, through a poly(chiral crown ether) membrane, racemic phenylglycine perchlorate was separated in 11%ee at the initial period but the selectivity almost disappeared after the initial period (1.5%ee) [98]. On the other hand, the interaction of a polymer of a HPLC chiral stationary phase with permeants is thought to be too weak to separate permeating racemates in the very short permeation path. Moreover, most of these polymers are crystalline and have no self-membrane-forming ability or their membranes are brittle. For example, since a chiral poly(amino acid) derivative [100] and cellulose carbamate [101] require a porous supporting membrane when they are used for membrane permeation, the polymers may be easily lost from the supporting membrane by applying pressure to enhance the permeation rate or by using solvent having only a weak affinity for the polymers. Therefore, in these types of membranes, permeation rates are low and it is difficult to maintain stability of the permeation performance.

4.3. New approach to design of optical resolution membrane

For an effective optical resolution membrane, the following requirements need consideration:

1. The membrane is a solid one having a self-membrane forming ability and its strength is high.
2. The permselectivity is high, that is, the enantiomeric excess (%ee) of the permeate is high.
3. The permeation rate is high, and is able to be enhanced by applying pressure.
4. The permselective ability is stable for a long time.
5. Many kinds of racemates are separated by the membrane.
6. A desired enantiomer is concentrated by selecting the chirality of the membrane polymer.

Since a self-supporting solid membrane can be easily fabricated in various forms and its durability is high, it can be applied to various production processes. Moreover, the permeation rate of a membrane having high durability can be enhanced by applying pressure. As mentioned above a liquid membrane shows low durability. Therefore, requirement (1) is the most fundamental.

Requirements (2) and (3) are important for all separation membranes. In general, when permselectivity increases, permeation rate decreases and vice versa. It is desirable to prepare membranes with both a high permeation rate and a high permselectivity for all kinds of separation including optical resolution.

Requirement (4) is also important. However, some of the reported solid membranes showed enantioselectivity only at an initial period as described above. If requirements (5) and (6) are accomplished in addition to (1)–(4), the membrane will become more valuable.

New approaches to macromolecular design for optical resolution solid membranes are as follows:

1. Membrane from polymer having bulky chiral group as pendant group;
2. Membrane having enantiomer recognition layer at the surface;
3. Membrane from polymer having chiral main chain.

4.3.1. Membrane from polymer having bulky chiral group as pendant group

4.3.1.1. Polysilylpropyne having bulky chiral groups. Optically active poly[1–[dimethyl(10-pinanyl)-silyl]-1-propyne]s [(+)- and (−)-poly(DPSP); **18**] were synthesized by homopolymerization of optically active 1-[dimethyl(10-pinanyl)silyl]-1-propyne[(−)-and (+)-DPSP] prepared from (−)- and (+)-β-pinene, respectively as shown in Scheme 1 [104]. In spite of the bulky pendant groups, the monomers were able to be polymerized by using $TaCl_5/Ph_3Bi$ as a catalyst to give high molecular weight polymers.

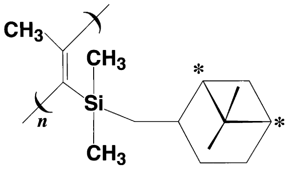

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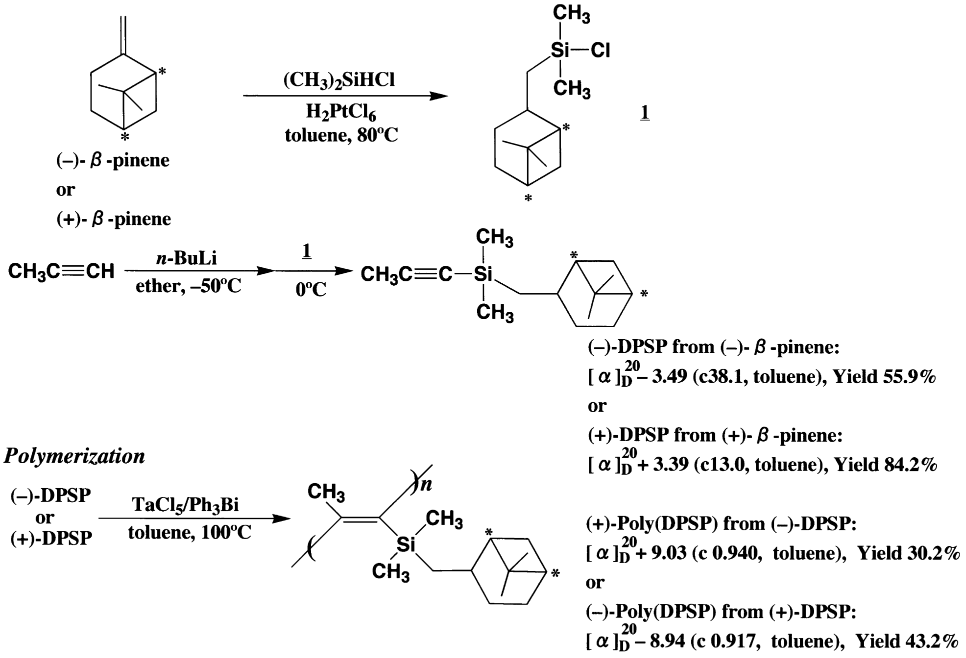
Fig. 9 shows the quantity (*Q*) of permeated (*R*)- and (*S*)-tryptophan (Trp) versus permeation time through a (+)-poly(DPSP) membrane in concentration-driven permeation (CP) when a methanol solution of racemic Trp was supplied [105]. The permeation through this membrane was enantioselective for (±)-Trp after an initial period. Especially at the initial period of this membrane permeation, the %ee of



Scheme 1.

permeated Trp was enhanced to 96%ee in the permeate from 0%ee in the feed. After the initial period, a moderate enantioselective permeation of 38%ee followed and which continued in a stable condition for more than 800 h. A similar enantioselective permeation behavior was observed in other racemates such as phenylalanine (Phe), valine (Val), and mandelic acid (Man). In other words, almost complete optical resolution occurred at the initial period (Fig. 10) and stable permeations with moderate enantioselectivity

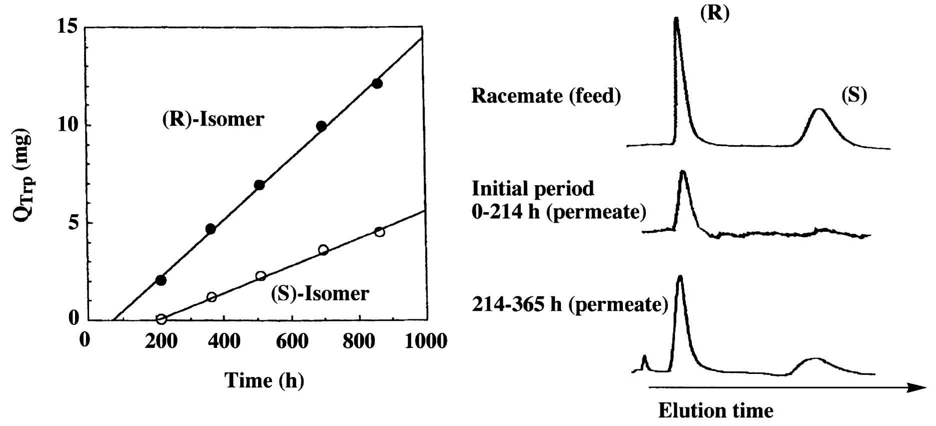


Fig. 9. Plots of quantity (Q_{Trp}) of permeated Trp from a racemate versus permeation time through (+)-poly(DPSP) membrane and HPLC chromatograms for the feed and permeates (feed 0.05 wt% methanol solution).

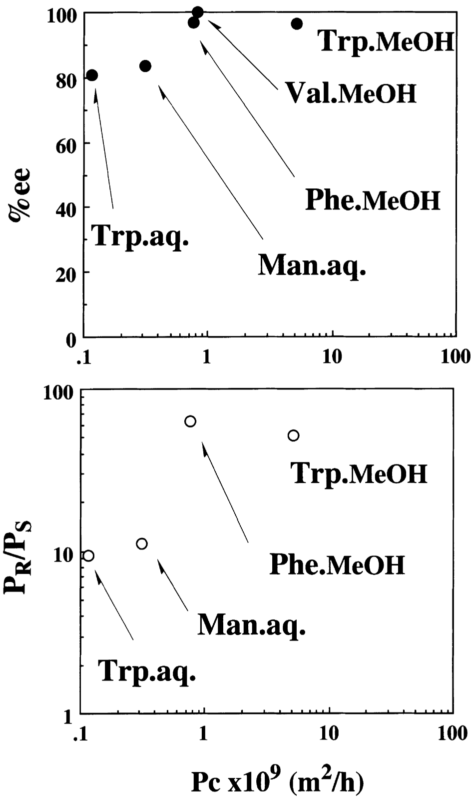


Fig. 10. Plots of permselectivity (%ee and P_R/P_S) versus permeability coefficient (P_c) for various racemates through (+)-poly-(DPSP) membrane at an initial period. Trp, tryptophan; Val, valine; Phe, phenylalanine; Man, mandelic acid; aq, aqueous solution; MeOH, methanol solution.

were observed after the initial period (Fig. 11). Moreover, this membrane could separate (±)-2-butanol (2-BuOH) enantioselectively. Since 2-BuOH is a small and less polar molecule and the direct separation of the racemate by chiral HPLC is impossible at present, this result is valuable and shows good enantioselective ability of this membrane. In summary, this solid membrane was found to be able to separate enantioselectively several kinds of racemates—α-amino acids, α-hydroxy acids, and alcohols—having different functional groups and molecular sizes. This finding suggests that enantioselective recognition is not caused by specific interaction between a certain functional group of a permeating racemate and that of the polymer such as in HPLC. To confirm this hypothesis, enantioselectivity in adsorption to a (+)-poly(DPSP) powder was examined for various racemates which could be enantioselectively separated by permeation. As a result, no enantioselective adsorption was detected. Therefore, it was confirmed that the reason for the enantioselective permeation was not selective adsorption or dissolution at the membrane surface and the mechanism was different from that of HPLC.

This membrane is dense and non-porous, and therefore bulky chiral pinanyl groups should be packed densely. Racemic permeants seem to permeate through a space surrounded by the bulky chiral pinanyl groups. Since permeants should contact strongly with the bulky chiral pinanyl groups during the permeation through the space, enantioselectivity is thought to occur in this diffusion process. The reason

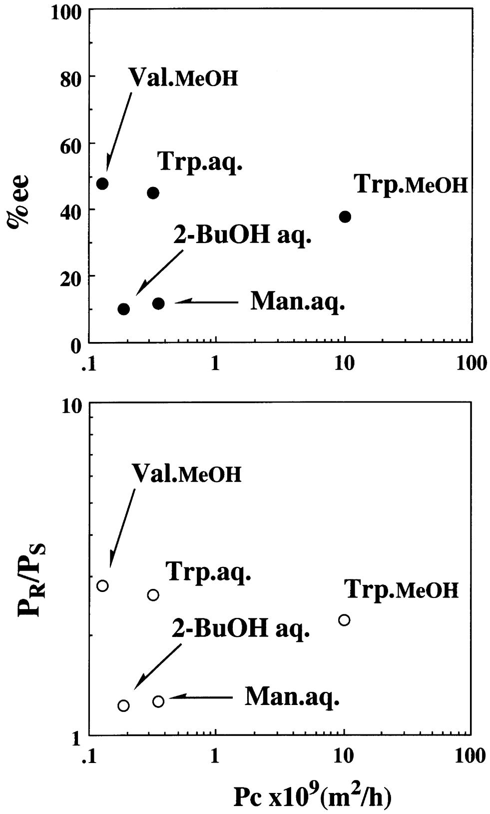


Fig. 11. Plots of permselectivity (%ee and P_R/P_S) versus permeability coefficient (P_c) for various racemates through (+)-poly(DPSP) membrane after the initial period. Trp, tryptophan; Val, valine; Phe, phenylalanine; Man, mandelic acid; aq, aqueous solution; MeOH, methanol solution.

for the enantioselective permeation for the wide range of the size of compounds may be the variability in size of the space among the chiral groups by molecular motion of the pendant groups. Accordingly, when suitable conditions are selected so as not to enlarge the space, optical resolution is achieved by the membrane.

Since this membrane is non-porous, it is possible to analyze the enantioselective permeation by the solution–diffusion mechanism, i.e. $P_c = D \times S$ where P_c is the permeability coefficient, D the diffusion coefficient, and S the solution coefficient. Table 10 summarizes the results of the analysis. The S ratios of the (*R*)- to the (*S*)-isomer (S_R/S_S) are close to unity, while the D ratios of the (*R*)- to the (*S*)-isomer (D_R/D_S) are close to the P_c ratios (P_R/P_S). Since the P_R/P_S values are governed by the D_R/D_S values, the enantioselectivity occurred not in the solution but in the diffusion process. In other words, the enantioselective permeation was achieved not by selective dissolution at the membrane surface but by selective diffusion through the chiral space formed by the pinanyl groups in the membrane. This result is consistent with the lack of enantioselective adsorption described above.

On the other hand, the P value was governed not by the D- but the S-value. The P_c and S values increased with an increase in $\sum F$ (hydrophobic fragmental constant) as shown in Fig. 12, indicating that

Table 10
Enantiomer permeation behavior of α-amino acids and 2-BuOH through (+)-poly(DPSP) membrane (*F* is the hydrophobic fragmental constant)

Solute ($\sum F$)	Solvent	P_c ($\times 10^{11}$ m^2 h^{-1})	P_R/P_S	D_R/D_S	S	S_R/S_S
Trp (2.31)	H_2O	27	2.6	2.5	28	1.0
Trp (2.31)	MeOH	1200	2.2	2.8	1800	0.8
Phe (2.24)	MeOH	210	3.3	3.6	540	0.9
Val (1.46)	MeOH	13	2.8	2.4	22	1.2
2-BuOH (0.74)	H_2O	21	1.2	1.3	26	1.0

racemates with higher affinity for the polymer permeated more rapidly. The factor for determining the selectivity was different from that of determining the permeation rate in this permeation.

In Trp permeation through the copolymer of (−)-DPSP with a small amount of TMSP, the enantioselectivity significantly decreased as shown in Fig. 13. This finding indicates that the space between the bulky pinanyl groups was enlarged by removing a small amount of the bulky chiral pinanyl groups. Therefore, the achievement of enantioselective permeation through this membrane needs a great number of densely packed chiral pendant groups. In order to enhance the density of the group, the introduction of additional chiral pinanyl groups was attempted by the cross-coupling reaction of lithiated α-methyl group of (+)-poly(DPSP) with chiral pinanyldimethylchlorosilanes but was unsuccessful. Therefore, (+)-poly(DPSP) has no extra space enough to introduce additional chiral pinanyl groups. Consequently, chiral pinanyl groups in (+)-poly(DPSP) were packed densely to a maximum degree, and the small spaces between these densely packed bulky chiral pendant groups may be necessary for highly enantioselective permeation.

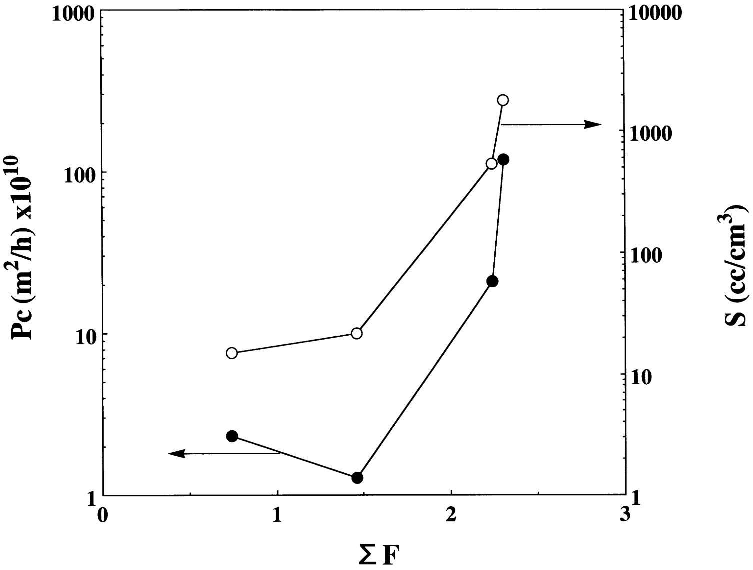


Fig. 12. Dependence of the permeability coefficient (P_c) and the solution coefficient (S) on $\sum F$ of permeant in CP, ($\sum F$) is the sum of hydrophobic fragmental constants.

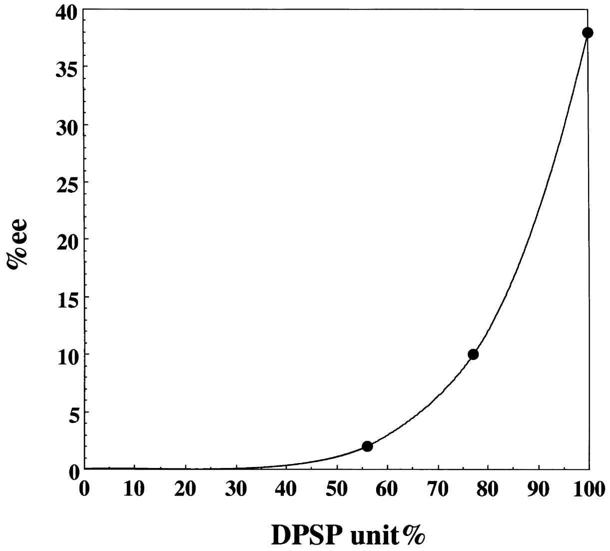


Fig. 13. Effect of DPSP unit % in copoly(DPSP/TMSP) on enantioselectivity in CP for Trp.

However, the permeation rates (P) in CP were very low ($P = 1$–50) and especially P of hydrophilic (±)-1,3-butanediol (1,3-BD) was nearly zero. In order to enhance the P value, the permeations in vapor state, i.e. evapomeation (EV) and pervaporation (PV), were tried [106]. By means of EV at 100°C, 1,3-BD permeated enantioselectively (42%ee at an initial period) with high P (=5100). It is interesting that enantioselective permeation occurred in the case of a vapor permeant. The P values in EV and PV were two orders of magnitude higher than those in CP. Since 1,3-BD is important as a chiral synthon and its direct separation by chiral HPLC is impossible, the achievement of this separation is of great value. After the initial period, the permeate with 17%ee with high P (=9200) was also obtained. PV of 1,3-BD showed higher enantioselectivity of 89%ee at the initial period and the P was high (=2200) and lower than that of EV.

In the case of PV of racemic 1,3-BD, (*R*)-1,3-BD permeated preferentially through a (+)-poly(DPSP) membrane, while (*S*)-1,3-BD permeated preferentially through a (−)-poly(DPSP) membrane. Therefore, a desired enantiomer can be concentrated by selecting the chirality of poly(DPSP).

Fig. 14 is a plot of %ee of the permeates versus logarithmic P for various racemates through (+)-poly(DPSP) membranes by several methods. The %ee values increased with a decrease in log P after an initial period (solid symbols). %ee values were higher in CP and lower in EV and PV, while P values were higher in EV and PV and lower in CP. In these permeations through (+)-poly(DPSP), a trade-off relationship was observed.

4.3.1.2. Polynorbornadiene having bulky chiral groups. We synthesized (+)-poly{2-[dimethyl(10-pinanyl)silyl]norbornadiene} [(+)-poly(DPSN); **19**] which had the same optically active pendant groups as that of (+)-poly(DPSP) and a more flexible main chain than that of (+)-poly(DPSP), and measured enantioselective permeability for (*RS*)-propranolol (Prp) and (*RS*)-tryptophan (Trp) through this polymeric membrane [107,108]. (−)-DPSN, synthesized from (−)-β-pinene and 2,5-norbornadiene, was

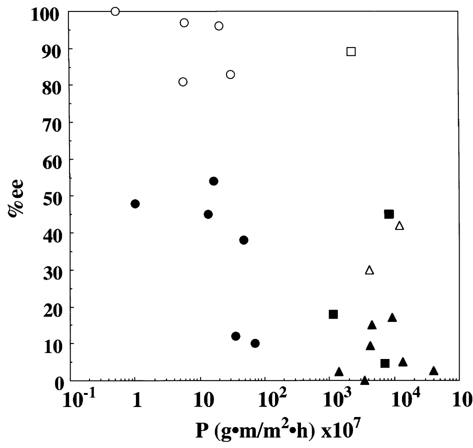


Fig. 14. A plot of %ee in the permeate versus log P for various racemates. (○, ●), CP; (△, ▲), EV; (□, ■), PV; (open symbol), an initial period; (solid symbol), after the period (from Ref. [105]).

polymerized by using WCl_6 as a catalyst and $(CH_3)_4Sn$ as a co-catalyst as shown in Scheme 2.

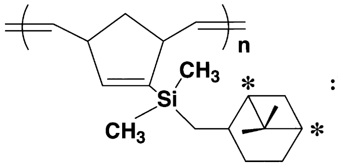


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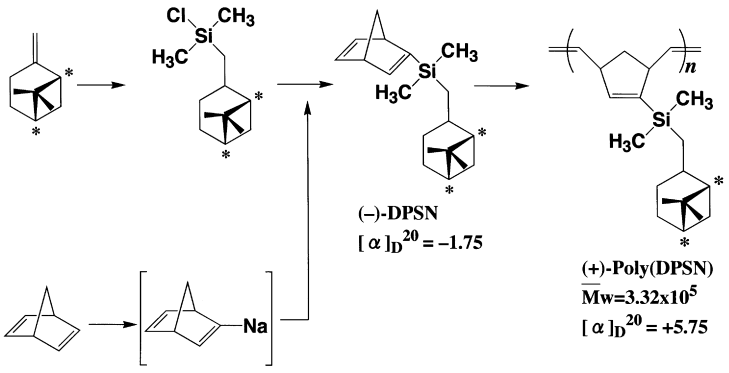
Fig. 15 shows the plots of quantity of permeated (*R*)- and (*S*)-Trp from aqueous racemic solution versus permeation time through (+)-poly(DPSN) membrane together with the result of (+)-poly(DPSP). The permeability coefficient ($P_c = 45.4$) of (+)-poly(DPSN) membrane for Trp was much higher than that (=2.72) of a (+)-poly(DPSP) membrane having higher selectivity. This may be because the main-chain of (+)-poly(DPSN) is more flexible than that of a (+)-poly(DPSP).



Scheme 2.

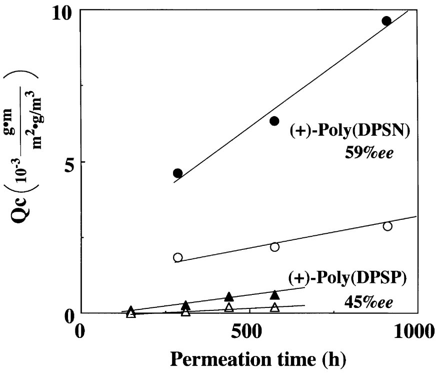


Fig. 15. Plots of normalized quantity (Q_c) of permeated (*R*)- (●, ▲) and (*S*)- (○, △)-tryptophan (Trp) from aqueous racemic solution (0.100 wt%) versus permeation time through (+)-poly(DPSN) (●, ○) and (+)-poly(DPSP) (▲, △) membrane (from Ref. [107]).

Fig. 16 shows the plot of quantity of permeated (*R*)- and (*S*)-Prp from racemic methanol solution versus permeation time through (+)-poly(DPSN) membrane. The (*R*)-(+)-isomer permeated preferentially. The %ee and P_c values were 45% and 2.80, respectively. This means that the (*R*)-isomer permeated 2.7 times faster than the (*S*)-isomer. This is the first example of optical resolution for Prp by membrane permeation. Moreover, this enantioselective permeation was stable for 2000 h. Since Prp is useful for medicine and one of hydrophobic compounds which were difficult to be separated by using a (+)-poly(DPSP) membrane, this attainment is significant.

4.3.2. Membrane having an enantiomer recognition layer at the surface

In order to obtain a new type of an optical resolution solid membrane containing a surface layer which can separate racemates enantioselectively, we prepared a new membrane consisting of a small amount of

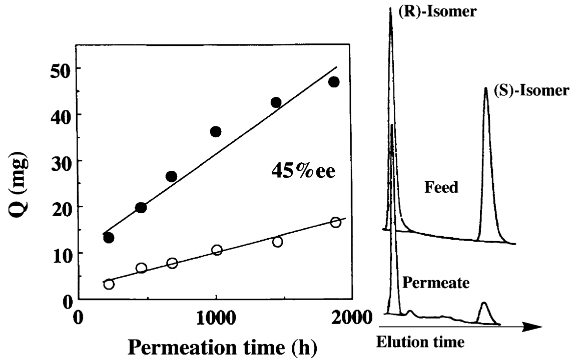


Fig. 16. Left: plots of quantity (*Q*) of permeated (*R*)- (●) and (*S*)- (○)-propranolol (Prp) from methanol racemic solution (0.500 wt%) versus permeation time through (+)-poly(DPSN) membrane. Right: chromatogram of HPLC of Prp: (above) racemic Prp in the feed; (below) Prp in the permeate during 650–1000 h. Column: CHIRALCELL-OD®; eluent: hexane/isopropanol, 19/1 (v/v) (from Ref. [107]).

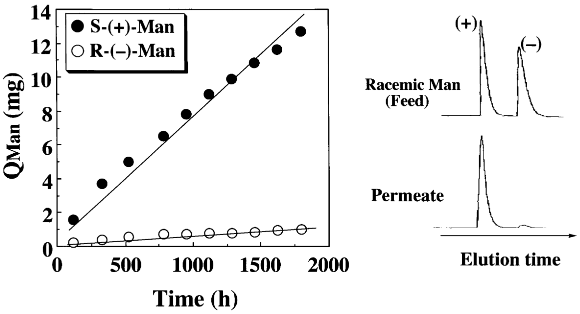
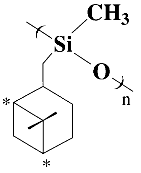


Fig. 17. Enantioselective permeation(CP) of 1.0 wt% aqueous DL-(±)-mandelic acid solution through 10.7 wt% (−)-OMPS/PMMA membrane. Left: Plots of the quantity of permeated mandelic acid (Q_{Man}) versus permeation time. Right: HPLC chromatogram (column: CHIRALPAK WH) of the feed and the permeate (from Ref. [109]).

(−)-oligo{methyl(10-pinanyl)siloxane} {(−)-OMPS, **20**} and poly(methyl methacrylate) (PMMA) [109].



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(−)-OMPS was synthesized by hydrolysis-polycondensation of methyl(10-pinanyl)dichlorosilane which had been prepared from dichlorosilane and (−)-β-pinene by hydrosilation. (−)-OMPS had a M_{w} of 1.20×10^3 corresponding to about 6-mer and could not form a self-supporting membrane because it was a viscous solid. A PMMA membrane whose surface was modified by (−)-OMPS was prepared by casting a 5% (w/v) THF solution of PMMA containing a small amount (10–12 wt%) of (−)-OMPS on a polytetrafluoroethylene sheet. Fig. 17 shows the results of the concentration-driven permeation of 1.0 wt% aqueous DL-Man solution through 10.7 wt% (−)-OMPS/PMMA. L-Man predominantly permeated through this membrane and the enantiomeric excess in the permeate was a high level of 85.4%ee. The enantioselective permeation continued for more than 1800 h. The permeation rate (*P*) was 7.31. *P* was enhanced by applying pressure (5 kg cm^{-2}) to 15.4 although the %ee dropped to 32.9% (Fig. 18). The enantioselective permeation was stable for 200 h.

The mechanism for the enantioselective permeation was discussed by examining the enantioselective adsorption of DL-Man and other racemic bodies to (−)-OMPS. Table 11 shows the enantioselectivities in the adsorption to (−)-OMPS and in the permeation through (−)-OMPS/PMMA. In all the three racemic bodies, (+)-isomers were selectively adsorbed and predominantly permeated, i.e. the isomers selected were identical in the adsorption and the permeation. Moreover, Man adsorbed with a high enantioselectivity permeated with a high enantioselectivity. These findings indicate that the enantioselectivity in the permeation was caused by the facilitated solution process at the membrane surface of the (+)-isomer which interacted more strongly with (−)-OMPS.

In order to investigate the effectiveness of the surface modified membrane, i.e. (−)-OMPS/PMMA, the permeation of DL-Man through another blend membrane which was not surface-modified, i.e. (−)-OMPS/polydimethylsiloxane (PDMS) was measured. (−)-OMPS/PDMS showed almost no

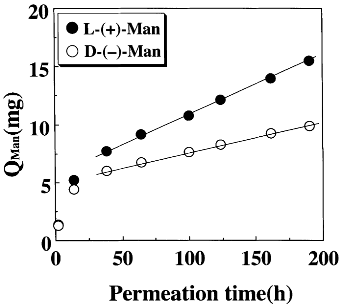
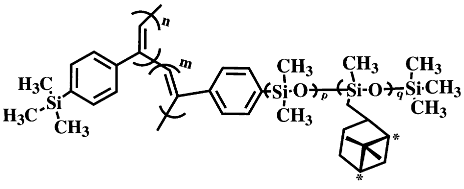


Fig. 18. Enantioselective permeation (PP) of 0.10 wt% aqueous DL-(±)-mandelic acid solution through 11.4 wt% (−)-OMPS/PMMA membrane by applying 5 kg cm^{-2} pressure. Plots of the quantity of permeated mandelic acid (Q_{Man}) versus permeation time (from Ref. [109]).

enantioselectivity. Therefore, it was found that (−)-OMPS is necessary to be present at the surface to realize the enantioselective permeation. In addition, (+)-PDPSP/PMMA of which (+)-PDPSP may be accumulated at the surface showed almost no enantioselectivity either. Since (+)-PDPSP was hardly enantioselective in adsorption, the enantioselective adsorption of (−)-OMPS was found to play an important role for the enantioselective permeation through (−)-OMPS/PMMA.

Since this membrane was able to separate other racemates, and several other surface-modified membranes were also found to have an enantioselectivity, and, in addition, these membranes need small amounts of expensive optically active compounds, this type of surface-modified membranes are good for optical resolution [110].

In the (−)-OMPS/PMMA membrane, since (−)-OMPS can bleed out from the membrane during permeation, its durability may be low. Moreover, the content of (−)-OMPS which can form an (−)-OMPS/PMMA membrane was low. In order to improve these defects, a graft copolymer ((−)-OMPS-graft-poly(PA), **21**) consisting of a polyphenylacetylene main chain and (−)-OMPS grafts was synthesized [111]. The membranes from the graft copolymer were tough and showed good permselectivity similar to the (−)-OMPS/PMMA membrane.



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4.3.3. Membrane from polymer having chiral main chain

4.3.3.1. Chiral poly(amino acid). Poly(L-glutamate)s having amphiphilic side chains of (*n*-nonylphenoxy)oligo(oxyethylene) (NON-PLG, **22**) possessed enantioselective permeability [100,112]. An almost complete optical resolution was attained. The permselectivity did not drop for more than 500 h as shown

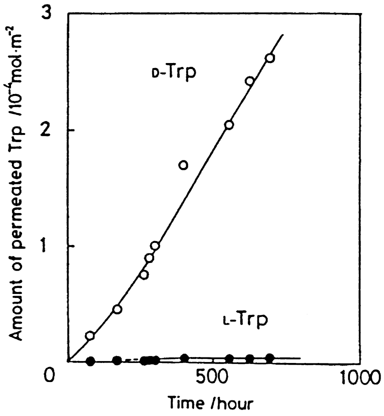
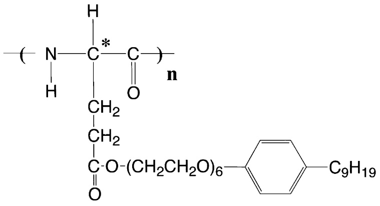


Fig. 19. Permeation behavior of D- and L-Trp from a racemate through NON-PLG (**22**) membrane at 34°C.

in Fig. 19. Since the polymer having α-helix structure formed a liquid crystal, the reason for the enantioselectivity was considered to be the ordered structure.



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In order to obtain a more highly permeable and enantioselective membrane we synthesized poly[γ-{3-(pentamethyldisiloxanyl)propyl} L-glutamate] (PSi2, **23**) containing a chiral backbone and flexible short side chains which can be easily affected by the backbone [113]. Poly(L-glutamic acid ester)s with 3-(pentamethyldisiloxanyl)propyl group (PSi2) were prepared by the ester exchange reaction of poly(γ-methyl L-glutamate) (PMLG) with the corresponding alcohol (ROH) using *p*-toluenesulfonic acid as a catalyst.

Table 11
Enantioselective adsorption of racemic bodies to (−)-OMPS (Man, mandelic acid; Val, valine; Phe, phenylalanine)

Racemate	Adsorption			Permeation[a]	
	Adsorbed compound/ (−)-OMPS (mol%)	Selectivity	%ee	Selectivity	%ee
Man	0.676	+	32.1	+	32.9
Val	0.215	+	2.6	+	0.5
Phe	0.253	+	5.9	+	4.0

[a] Pressure-driven permeation through 10–12 wt% OMPS/PMMA membrane.

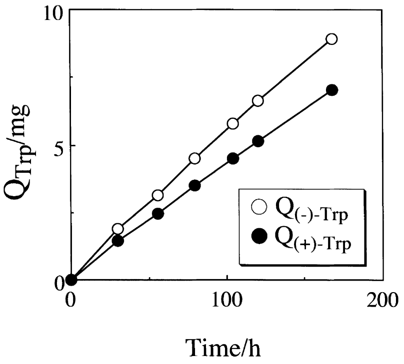

Fig. 20. Plots of quantity (Q_{Trp}) of (+)- and (−)-tryptophan permeated through PSi2(44) membrane versus permeation time (from Ref. [113]).

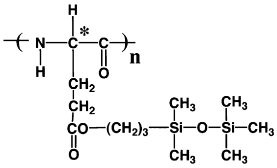

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Fig. 20 is a plot of permeated (+)- and (−)-tryptophan versus permeation time through PSi2(44) (44% substitution degree) when racemic tryptophan was fed. This membrane showed enantioselective permeability for (±)-tryptophan. By this membrane permeation %ee of (±)-tryptophan was enhanced to 16%ee in the permeate from 0%ee in the feed. This enantioselective permeation was stable and continued for more than 160 h. This enantioselective permeability was also observed in another membrane; PSi2(64) (64% substitution degree). The two membranes had a similar permeation behavior, i.e. these regions of substitution degree hardly affected the behavior. However, PSi2 membranes having lower substitution degree than 44% showed lower permeation rates. Fig. 21 shows the effect of the substitution degree on the permeation behavior. With an increase in the degree from 12 to 44%, the permeation rate increased with retention of enantioselectivity (13–15%ee). This may be because the siloxane region

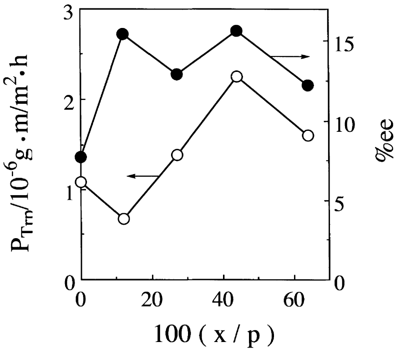


Fig. 21. Plots of P_{Trp} and %ee versus the content of the siloxane short side chain in PSi2 membrane (from Ref. [113]).

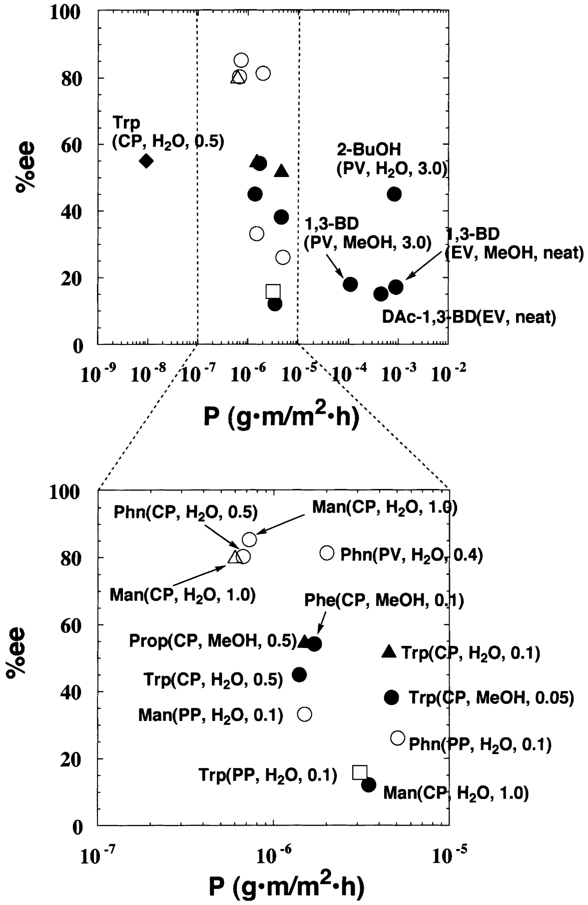


Fig. 22. Enantioselective permeation of various racemates through various optical resolution membranes. Descriptions in the figure indicate “solute (method, solvent, concentration)”. ●, (+)-Poly(DPSP) (**18**); ▲, (−)-poly(PNBD) (**19**); ○, (−)-OMPS (**20**)/PMMA; △, (−)-OMPS-graft-poly(PA) (**21**); □: (+)-poly(Si2LG) (**23**); ◆, (−)-poly(MtCPA) (**24**); CP, concentration-driven permeation; PP, pressure-driven permeation; PV, pervaporation; EV, evapomeation.

affords an important permeation route. All PSi2 membranes showed higher enantioselectivity than PMLG. This reason is not clear at present, but perhaps its flexible siloxane side chains may eliminate microsized defects in PMLG membrane.

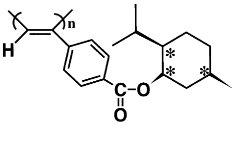
The enantioselectivities of PSi2 membranes were lower than those of NON-PLG, but the permeation rates were 10^5 higher than that of NON-PLG. The high permeability of PSi2 membrane was due to the applied pressure, and this membrane could resist a 10 kg cm^{-2} pressure difference. On the other hand, NON-PLG does not seem to have strength enough to resist the pressure difference nor does it seem to improve the low permeation rate. However, NON-PLG showed a very high enantioselective permeability (about 100%ee). It was reported that this high enantioselective permeability was attributed to a highly ordered structure of the rigid side chains induced by its chiral helical main chain. On the other hand, the flexible side chains of PSi2 do not seem to have a highly ordered structure. This may be the reason why PSi2 membranes had a lower permselectivity. PSi2 membranes had a stable enantioselective permeation for more than 160 h. This may be owing to the soft property of the siloxane side chains.

In order to obtain information on the mechanism of the enantioselective permeation, adsorption of (±)-tryptophan or (±)-mandelic acid to PSi2 was examined. As a result, PSi2 exhibited enantioselective adsorption for tryptophan and mandelic acid, and (+)-isomer was enantioselectively adsorbed. This selectivity was opposite to that of the permeation. Therefore, the permeation of (+)-isomer was thought to be suppressed by the relatively higher interaction with PSi2 resulting in the selective permeation of (−)-isomer.

As described above, PSi2 membrane had an α-helix when it was cast by using 1,2-dichloroethane similar to PMLG, and an α-helix along with a small amount of random structure when it was cast by using trifluoroacetic acid. In order to investigate if this high-order structure is effective for the enantioselective permeation, permeation through two kinds of PSi2 membranes, which contained a different high-order structure, were measured. A membrane prepared using 1,2-dichloroethane and one using trifluoroacetic acid had almost the same permeation performance. This finding suggests that the α-helix content does not significantly affect the permeation performance. Therefore, the high-order structure was not found to affect the enantioselective permeation. The enantioselectivity may be ascribed to the asymmetric carbons and not to the α-helix.

As shown in Fig. 21, with an increase in the substitution degree of the siloxane side chain, the permeation rate of tryptophan increased. This is clearly because the siloxane region constituted highly continuous domains and became an important permeation route. Therefore, the aqueous tryptophan solution mainly permeated this siloxane domain, which had no asymmetric centers. Nevertheless, (±)-tryptophan was separated enantioselectively in the permeation. This finding suggests that this siloxane region had an ability for enantioselective recognition, i.e. this region was influenced more or less by its chiral backbone structure. If this region had no ability for enantioselective recognition and only the backbone region had the ability, the permeation rate would increase but the enantioselectivity would decrease with an increase in the siloxane side chain content. However, the permeation rate increased and the selectivity did not drop.

4.3.3.2. Chiral polyphenylacetylene. Polymerization of *p*-(L-(−)-menthoxycarbonyl)phenylacetylene $\{[\alpha]_D^{20} = -68.8$ (c 0.580, $CHCl_3$) $\}$ by using $[Rh(norbornadiene)Cl]_2$ as a polymerization catalyst led to (−)-poly[*p*-(L-(−)-4-menthoxycarbonyl)phenylacetylene]s, which exhibited a much higher optical rotation { poly(MtCPA); **24**, $[\alpha]_D^{20} = -605$ (c 1.0, $CHCl_3$)} [114,115]. The CD spectrum showed a Cotton effect with a high molar ellipticity ($° cm^2 dmol^{-1}$) of − 71 000 (at 272 nm) and + 37 000 (at 310 nm), which were one order of magnitude higher than that of known chiral polyacetylenes.



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The important features of poly(MtCPA) having a high stereoregularity were its very high molecular weight ($M_w > 10^6$) and good solubility. Polyacetylenes having a high molecular weight and high stereoregularity generally tend to be insoluble. However, poly(MtCPA)s were easily soluble in benzene, toluene, xylene, carbon tetrachloride, 1,2-dichloroethane, chloroform and tetrahydrofuran. Therefore this polymer was easily fabricated to a tough membrane by a solvent-casting method. The CD spectrum of the polymer in the membrane was similar to that in solution, indicating that the polymer had also a helical conformation with an excess of one sense in a solid membrane.

When 0.5 wt% DL-tryptophan aqueous solution was fed, the %ee of the permeate through the membrane was 54–55%ee for 600–3000 h showing a D-(+)-enantiomer selective permeability ($P_c = 0.018$), and when 0.05 wt% DL-tryptophan methanol solution was used, %ee was 8–15%ee for 240–600 h ($P_c = 54$). Since this polymeric membrane is very tough and flexible, the low permeability will be improved by applying pressure and using a membrane with a larger area and a lesser thickness.

Fig. 22 summarizes the enantioselective permeation behavior through new membranes described above. Trade-off relationship was observed in this case similar to the case of oxygen permselective membranes. Other approaches have also been reported [116–118].

5. Membrane with permeability controlled by external stimulation

5.1. Membrane with controlled permeability

5.1.1. Liquid membranes and bimolecular membranes

Membranes whose permeabilty can be controlled by external stimulation were realized mainly in the case of a liquid membrane. Shinkai et al. achieved a light controlled facilitated transport of potassium ion and a light controlled active transport of alkaline earth metal ion by using liquid membranes containing a photoresponsive crown ether [7,8]. Okahata et al. reported that reversibly controlled transports of sodium chloride through a bimolecular membrane were observed by applying an electric field or a temperature change [119]. The stabilization or fixation of these membranes were investigated by using polymer–liquid crystal composite membranes or porous membranes [120,121].

5.1.2. Solid membranes

Kinoshita et al. reported a pH or photo-controlled permeation through poly(amino acid derivatives) membranes. The pH control was based on swelling in the transition of α-helix to random coil of the main chain, and the photo-control was caused by the formation of polyanions of rose groups introduced to the side chain followed by swelling [122–124].

Ikada et al. found a water permeation reversibly controlled by a temperature change. This membrane was a porous membrane with a polymer, showing transition phenomenon at a temperature, as grafts in the pores. This change in permeation rate was thought to be caused by opening and closing of the pores by shrinking and extending of the grafted polymer on the transition temperature [125]. Saito et al. controlled the flux by using the change in swelling depending on temperature of a temperature-responsive polymer gel membrane [126].

5.2. Membrane with controlled permselectivity

Most of permeability controlled membranes described in Section 5.1 were a water membrane containing crown ether with responsive groups or a polymer membrane which can swell in water. In these membranes, water played an important role. However, these membranes cannot control the permselectivity.

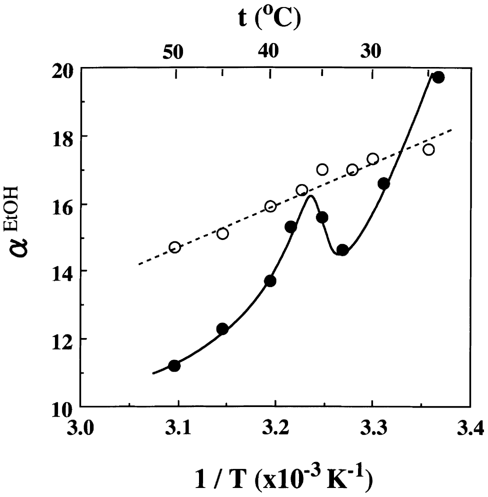

Fig. 23. Plots of α^{EtOH} of PDMS-based blend membrane containing 5.3 wt% copoly (IPAA/FA) (●) or 5.8 wt% polyFA (○) versus 1/*T* (from Ref. [127]).

We achieved temperature-controlled ethanol permselectivity through a blend membrane consisting of 5.3 wt% copoly(*N*-isopropylacrylamide/1H,1H,2H,2H-perfluorododecyl acrylate) and polydimethylsiloxane as shown in Fig. 23. This behavior was due to the thermal transition of the copolymer being accumulated at the membrane surface [127].

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References

[1] Yamaguchi S, Nakao S. Kimura. Macromolecules 1991;24:5522.
[2] Nakagawa T. Makugijutsu no Kiso, Tokyo: Kitamishobou, 1983. p. 59.
[3] Jhonson M, Baker RW, Matson SL, Smith KL, Roman LC, Tuttle F, Lonsdale HK. J Membr Sci 1987;31:31.
[4] Newcomb M, Helgeson RC, Cram DJ. J Am Chem Soc 1974;96:7367.
[5] Nishide M, Ohyanagi O, Okada E. Tsuchida. Macromolecules 1986;19:494.
[6] Nishide H. Membrane 1992;17:115.
[7] Shinkai S, Ogawa T, Kusano Y, Manabe O, Kikukawa K, Goto T, Matsuda T. J Am Chem Soc 1982;104:1960.
[8] Shinkai S, Minami T, Kusano Y, Manabe O. J Am Chem Soc 1982;104:1967.
[9] Kikuchi H, Hattori J, Mori Y, Kajiyama T. Kagakukougaku Ronbunshu 1989;15:617.
[10] Shinkai S, Nakamura S, Tachiki S, Manabe O, Kajiyama T. J Am Chem Soc 1985;107:3363.
[11] Kajiyama T, Washizu S, Ohmori Y. J Membr Sci 1985;24:73.
[12] Robeson LM. J Membr Sci 1991;62:165.
[13] Ward III WJ, Browall WR, Salemme RM. J Membr Sci 1976;1:99.
[14] Asakawa S, Saitou Y, Kawato M, Itoh Y, Tsuchiya S, Kanda K. Natl Tech Report 1983;29:93.

[15] Kawakami Y, Aoki T, Hisada H, Yamamura Y, Yamashita Y. Polym Commun 1985;26:133.
[16] Kawakami Y, Karasawa H, Aoki T, Yamamura Y, Hisada H, Yamashita Y. Polym J 1986;17:1159.
[17] Kawakami Y, Kamiya H, Yamashita Y. J Polym Sci: Polym Symp 1986;74:291.
[18] Kawakami Y, Kamiya H, Yamashita Y. J Polym Sci 1987;A25:3191.
[19] Kawakami Y, Hisada H, Yamashita Y. J Polym Sci 1988;A26:1307.
[20] Kawakami Y, Aoki T, Yamashita Y. Kobunshi Ronbunshu 1986;43:741.
[21] Nagase Y, Naruse A, Matsui K. Polymer 1990;31:121.
[22] Nagase Y, Mori S, Egawa M, Matsui K. Makromol Chem 1990;191:2413.
[23] Nagase Y, Ochiai J, Matsui K, Uchikura M. Polymer 1988;29:740.
[24] Kiyotukuri T, Tsutsumi M, Ayama K, Nagata M. J Polym Sci 1986;A25:1591.
[25] Aoki T, Yamamoto Y, Shin K, Oikawa E. Makromol Chem Rapid Commun 1992;13:525.
[26] Nakajina T, Kinoshita T, Takizawa O, Tsujita Y. Kobunshi Ronbunshu 1990;47:415.
[27] Kawakami Y, Karasawa H, Kamiya H, Aoki T, Yamashita Y. Polym J 1986;18:237.
[28] Nagasaki Y, Kurosawa K, Suda M, Takahashi S, Tsuruta T, Ishihara K, Nagase Y. Makromol Chem 1990;191:2103.
[29] Aoki T, Kuribayashi T, Oikawa E. The 62nd Shuukinenkai Kouen Yokoushu III, Tokyo: The Chemical Society of Japan, 1991. p. 920.
[30] Aoki T, Kobayashi H, Oikawa E. Polym Bull 1995;34:133.
[31] Masuda T, Iguchi Y, Tang B-Z, Higashimura T. Polymer 1988;29:2041.
[32] Takada K, Matsuya H, Masuda T, Higashimura T. J Appl Polym Sci 1985;30:1605.
[33] Odani S. Kobunshi 1988;37:452.
[34] Nakagawa T. Kobunshi 1988;37:832.
[35] Ichiraku Y, Stern SA, Nakagawa T. J Membr Sci 1987;34:5.
[36] Asakawa S, Saitou Y, Seki M. Polym Prepr, Jpn 1987;36:1952.
[37] Tsuchihara K, Masuda T, Higashimura T. Macromolecules 1992;25:5816.
[38] Nagase Y, Mori S, Matsui K, Uchikawa M. J Polym Sci 1988;A26:3131.
[39] Aoki T, Nakahara H, Hayakawa Y, Kokai M, Oikawa E. J Polym Sci 1994;A32:849.
[40] Aoki T, Nakahara H, Oikawa E. Polym Prepr, Jpn 1993;42:4036.
[41] Hayakawa Y, Nishida M, Aoki T, Muramatsu H. J Polym Sci 1992;A30:873.
[42] Kita H, Sakamoto T, Tanaka K, Okamoto K. Polym Prepr, Jpn 1987;36:1931.
[43] Brandup J, Immergut EH. Polymer handbook. New York: Wiley, 1989. p. VI/440.
[44] Chiou JS, Paul DR. Ind Engng Chem Res 1988;27:2161.
[45] Lee YT, Iwamoto K, Seno M. J Membr Sci 1990;49:85.
[46] Sakai T, Takenaka H, Torikai E. J Membr Sci 1987;31:227.
[47] Aoki T, Watanabe J, Ishimoto Y, Oikawa E, Hayakawa Y, Nishida M. J Fluorine Chem 1992;59:295.
[48] Stern SA, Shah VM, Hardy BJ. J Polym Sci: Polym Phys Ed 1987;25:1263.
[49] Kawakami Y, Aoki T, Hisada H, Yamamura Y, Yamashita Y. Polym Commun 1985;26:133.
[50] Nagase Y, Ochiai J, Matsui K, Uchikura M. Polymer 1988;29:740.
[51] Aoki T, Toyoshima Y, Oikawa E. Polym J 1994;26:1142.
[52] Coleman MR, Koros WJ. J Membr Sci 1990;50:285.
[53] Kim TH, Koros WJ, O'Brien KC. J Membr Sci 1988;37:45.
[54] Stern SA, Mi Y, Yamamoto H. J Polym Sci 1989;B27:1887.
[55] Nagase Y, Ochiai J, Matsui K, Uchikura M. Polym Commun 1988;29:10.
[56] Kagawa S, Ishikawa R, Moriguchi I, Teraoka Y. Chem Lett 1989:1817.
[57] Terada I, Haraguchi T, Kajiyama T. Polym J 1986;18:529.
[58] Inagaki N, Tanaka S, Park MS. J Appl Polym Sci 1990;40:143.
[59] Kita H, Shigekuni M, Kawafune I, Tanaka K, Okamoto K. Polym Bull 1987;21:371.
[60] Inagaki N, Katsuoka H. J Membr Sci 1987;34:297.
[61] Kawakami M, Yamashita Y, Iwamoto M, Kagawa S. J Membr Sci 1984;19:249.
[62] Shin K, Aoki T, Oikawa E. Koubunshi Ronbunshu 1995;52:1.
[63] Ohno Y. The 27th Koubunrikinouzairyou Kenkyukai-kouza Kouen Youshishu, Tokyo: The Society of Polymer Science, Japan, 1991. p. 20.
[64] Mizoguchi K, Hirose T, Kamiya Y. Polym Prepr, Jpn 1991;40:1484.

[65] Otsu T, Yoshioka M. Makromol Chem 1992;193:2283.
[66] Ichikawa M, Katagiri S, Yamanaka T, Ohyanagi M, Ikeda K, Sekine Y. Polymer 1987;28:269.
[67] Aoki T, Itoh K, Shin K, Oikawa E. Polym Prepr, Jpn 1994;43:2259.
[68] Mi Y, Stern SA. J Polym Sci 1991;B29:389.
[69] Aoki T, Kobayashi H, Oikawa E. Polym Prepr, Jpn 1994;43:2257.
[70] Kajiyama T, Washizu S, Ohmori Y. J Membr Sci 1985;24:73.
[71] Kunitake T, Higashi N, Kajiyama T. Chem Lett 1984:717.
[72] Kawakami Y, Aoki T, Yamashita Y. Polym Bull 1987;17:293.
[73] Chen G, Griesser HJ, Mau AWH. J Membr Sci 1993;82:99.
[74] Tsuchida E, Nishide H, Ohyanagi M, Kawakami H. Macromolecules 1987;20:2312.
[75] Nishide H, Ohyanagi M, Okada O, Tsuchida E. Polym J 1987;19:839.
[76] Nishide H, Ohyanagi M, Okada O, Tsuchida E. Macromolecules 1986;19:494.
[77] Nishide H, Kawakami H, Sasame Y, Ishiwata K, Tsuchida E. J Polym Sci 1992;A30:77.
[78] Nishide H, Kawakami H, Nishihara S, Tsuda K, Suzuki T, Tsuchida E. Polym Adv Technol 1993;4:17.
[79] Nishide H, Kuwahara M, Ohyanagi M, Funada Y, Kawakami H, Tsuchida E. Chem Lett 1986:43.
[80] Aoki T, Shin K, Oikawa E. Polym J 1996;28:106.
[81] Shin K, Aoki T, Oikawa E. Macromol Rapid Commun 1995;16:599.
[82] Baker RW, Blume I. Chemtech 1986;16:232.
[83] Aoki T, Oikawa E, Hayakawa Y, Nishida M. J Membr Sci 1991;57:207.
[84] Harada J, Nozaki M. Polym Prepr, Jpn 1987;36:1940.
[85] Longsam M, Anand M, Karwacki EJ. Gas separation and purification 1988;2:163.
[86] Longsam M, Robeson LM. Polym Prepr 1988;29:112.
[87] Nagase Y, Mori S, Ishihara K, Matsui K, Uchikura M. Polym Prepr, Jpn 1986;35:2046.
[88] Nagase Y, Matsui K. Polym Prepr, Jpn 1987;36:3357.
[89] toHenneppe HJC, Bargeman D, Mulder MHV, Smalder CA. J Membr Sci 1987;35:39.
[90] Kashiwagi T, Okada T, Okita K. J Membr Sci 1988;36:353.
[91] Ishihara K, Kogure R, Matsui K. Kobunshi Ronbunshu 1986;43:779.
[92] Nakamura M, Samejima S, Kawasaki T. J Membr Sci 1988;36:343.
[93] Ishida H, Tamura M, Sekiya A. Kobunshi Ronbunshu 1990;47:139.
[94] Ishihara K, Matsui K. J Appl Polym Sci 1987;34:437.
[95] Aoki T, Toyoshima Y, Yoshizawa T, Oikawa E. Polym Commun 1992;33:662.
[96] Aoki T, Toyoshima Y, Yamagiwa Y, Oikawa E. Kobunshi Ronbunshu 1992;49:791.
[97] Aoki T, Yamagiwa K, Oikawa E. Polym Prepr, Jpn 1992;41:2664.
[98] Kakuchi T, Yokota T, Yokota K. Polym J 1990;22:199.
[99] Higuchi A, Hara M, Horiuchi T, Nakagawa T. J Membr Sci 1994;93:157.
[100] Maruyama A, Adachi N, Takatsuki T, Torii M, Sanui K, Ogata N. Macromolecules 1990;23:2748.
[101] Yashima E, Noguchi J, Okamoto Y. J Appl Polym Sci 1994;54:1087.
[102] Nakagawa T, Toyokawa Y, Abe M, Higuchi A. Macromol Symp 1994;84:209.
[103] Ishihara K, Suzuki N, Matsui K. Nippon Kagaku Kaishi 1987:446.
[104] Aoki T, Shinohara K, Oikawa E. Makromol Chem: Rapid Commun 1992;13:565.
[105] Aoki T, Shinohara K, Kaneko T, Oikawa E. Macromolecules 1996;29:4192.
[106] Shinohara K, Aoki T, Oikawa E. Polymer 1995;36:2403.
[107] Aoki T, Ohshima M, Shinohara K, Kaneko T, Oikawa E. Polymer 1997;38:235.
[108] Aoki T, Ohshima M, Shinohara K, Kaneko T, Oikawa E. Polym Prepr, Jpn 1995;44:2680.
[109] Aoki T, Maruyama A, Shinohara K, Oikawa E. Polym J 1995;27:547.
[110] Aoki T, Maruyama A, Oikawa E. Polym Prepr, Jpn 1995;44:311.
[111] Aoki T, Suzumura K, Shinohara K, Kanako T, Oikawa E. Polym Prepr, Jpn 1996;45:398.
[112] Maruyama A, Adachi N, Takatsuki T, Sanui K, Ogata N. Nippon Kagaku Kaishi 1990:1178.
[113] Aoki T, Tomizawa S, Oikawa E. J Membr Sci 1995;99:117.
[114] Aoki T, Kokai M, Shinohara K, Oikawa E. Chem Lett 1993:2009.
[115] Aoki T, Kokai M, Oikawa E. Polym Prepr, Jpn 1994;43:969.
[116] Shinbo T, Yamaguchi T, Yanagishita H, Sakai K, Kitamoto D, Sugiura M. J Membr Sci 1993;84:241.

[117] Masawaki T, Sanui M, Tone S. J Chem Engng, Jpn 1992;25:33.
[118] Yoshikawa M, Izumi J, Kitao T, Koya S, Sakamoto S. J Membr Sci 1995;108:171.
[119] Okahata Y, Hachiya S, Ariga K, Seki T. J Am Chem Soc 1986;108:2863.
[120] Kumano A, Niwa O, Kajiyama T, Takayanagi M, Kano K, Shinkai S. Chem Lett 1983:1327.
[121] Okahata Y. Acc Chem Res 1986;19:57.
[122] Kikuchi T, Kinoshita T, Takizawa A, Tsujita Y, Oya M, Iwatsuki M. Polym Prepr, Jpn 1989;38:3913.
[123] Kinoshita T, Takizawa O, Tsujita Y, Ishikawa G. Kobunshi Ronbunshu 1986;43:827.
[124] Sato M, Kinoshita T, Takizawa A, Tsujita Y. Polym J 1989;21:369.
[125] Iwata H, Oodate M, Uyama Y, Amemiya H, Ikada Y. J Membr Sci 1991;55:119.
[126] Tsuji T, Konno M, Saito S. J Chem Engng, Jpn 1990;23:447.
[127] Aoki T, Yamagiwa K, Yoshino E, Oikawa E. Polymer 1993;34:1538.