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SHORT COMMUNICATIONS

Optical Resolution by Use of Surface-Modified Poly(methyl methacrylate) Membrane Containing (−)-Oligo{methyl(10-pinanyl)siloxane}

Toshiki AOKI,† Akira MARUYAMA, Ken-ichi SHINOHARA,* and Eizo OIKAWA

Department of Chemistry and Chemical Engineering, Faculty of Engineering, Niigata University, Ikarashi 2-8050, Niigata 950-21, Japan
** Graduate School of Science and Technology, Niigata University, Ikarashi 2-8050, Niigata 950-21, Japan*

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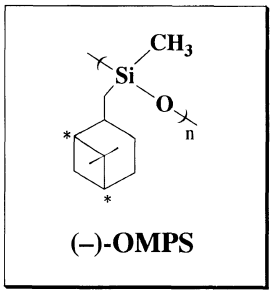
Since optically active compounds are closely related to biological and pharmacological activity, the development of an effective method for producing the compounds is very significant. Although there are several conventional methods for optical resolution such as diastereoisomer method and high-performance liquid chromatographic method, only a very small amount of the optically active compound can be treated in one operation of these methods. On the other hand, an optical resolution membrane is expected to realize the treatment of a large amount of racemic compounds. Some liquid membranes for optical resolution were reported[1] but there are only a few reports on solid membranes[2] which is more stable and practical. We reported that a (+)-poly[1-{dimethyl(10-pinanyl)silyl}-1-propyne]{(+)-PDPSP} membrane[3] and a membrane from poly(γ-methyl L-glutamate) derivative with disiloxane side chains[4] were able to separate DL-tryptophan enantioselectively in high optical purity (%e.e. = 86.1) and high permeation rate ($P = 3.12 \times 10^{-6}$ g·m·m^{-2}·h^{-1}), respectively. However, the former and the latter showed low P and low %e.e., respectively.

In this communication, we now report a new type of an optical resolution solid membrane containing a surface layer which can separate racemic body enantioselectively. Such a membrane is expected to be prepared by casting the solution of the binary blend of a small amount of optically active siloxane compounds and a more polar polymer. In this membrane, the siloxane compounds are likely to be accumulated at the surface owing to its lower surface energy. We reported the preparation of such surface modified membranes and their oxygen and ethanol permselectivity.[5-7]

In order to realize such a new type of an optical resolution solid membrane, we prepared a new membrane consisting of a small amount of (−)-oligo{methyl(10-pinanyl)siloxane}{(−)-OMPS, Scheme 1} and poly(methyl methacrylate) (PMMA) and measured its enantioselective permeability for DL-mandelic acid

† To whom all correspondence should be addressed.



Scheme 1. Chemical structure of (−)-OMPS.

(Man). In addition, to investigate its separation mechanism, the adsorption of racemic bodies on (−)-OMPS and the permeation of DL-Man through a surface-unmodified membrane were examined.

(−)-OMPS was synthesized by hydrolysis-polycondensation of methyl(10-pinanyl)dichlorosilane which had been prepared from dichlorosilane and (−)-β-pinene by hydrosilation. The M_n of (−)-OMPS determined by using vapor pressure osmometer was 1.20×10^3 corresponding to about 6-mer, and its $[\alpha]_D$ in tetrahydrofuran (THF) was −1.83. (−)-OMPS was soluble in various organic solvents such as chloroform and THF, but it could not form a self-supporting membrane because it was 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. The casting solvent was evaporated for 12 h at room temperature. The formed membrane was detached from the sheet and then was dried *in vacuo* for 24 h at room temperature. This membrane was designated (−)-OMPS/PMMA. Table I shows the characterization of the surface of the blend membrane. The increase in the contact angle value from 81.4° to 93.5° suggests that (−)-OMPS was accumulated at the surface. In addition, since the absorbance ratio of 1072 cm^{-1} to 1712 cm^{-1} ($A_{\nu Si-O}/A_{\nu C=O}$) was *ca.* 600 times larger in attenuated total reflection infrared spectrum (ATR-IR) than that in transmittance IR, the accumulation of (−)-OMPS at the surface was confirmed.

Table I. Characterization of the surface of (−)-OMPS/PMMA

Membrane	Contact angle of water/ degree	$A_{\nu Si-O}/A_{\nu C=O}$[a]	
		ATR[b]	TRANS[c]
10 wt% (−)-OMPS/PMMA[d]	93.5	3.62	0.00581
PMMA	81.4	—	—

[a] $A_{\nu Si-O}$ and $A_{\nu C=O}$ are the absorbance at 1072 cm^{-1} in (−)-OMPS, and the absorbance at 1712 cm^{-1} in PMMA, respectively. [b] ATR is attenuated total reflection FT-IR using KRS-5 prism at an incident angle of 55°. [c] TRANS is transmittance IR. [d] (−)-OMPS, (−)-oligo{methyl(10-piranyl)siloxane}; PMMA, poly(methyl methacrylate).

A concentration-driven permeation of 1.0 wt% aqueous DL-Man solution was measured using a two chamber glass cell and a pressure-driven (5 $kg \cdot cm^{-2}$) permeation of 0.1 wt% aqueous racemic body solution of Man, valine (Val), or phenylalanine (Phe) was measured at 25°C using a batch type reverse osmosis apparatus manufactured by AKICO. Permeation rates (P) were determined by weighing the permeated Man after the solvent was evaporated.

$$P(g \cdot m \cdot m^{-2} \cdot h^{-1}) = (Q \times L)/(A \times t)$$

where Q is the quantity of the solute permeated and t is the permeation time, and L and A are the thickness and area of the membrane, respectively. Enantiomeric excess (%e.e.) of the permeated solution was determined by high performance liquid chromatography (HPLC) with a CHIRALPAK WH column for Man and CROWNPAK CR for Val and Phe purchased from Daicel chemical industries, Ltd. As a controlled experiment, a solution of a given concentration similar to that of the permeate was allowed to stand for the same time under the same conditions as the permeation experiment. As a result, no change in %e.e. was observed.

The adsorption experiments of several race-

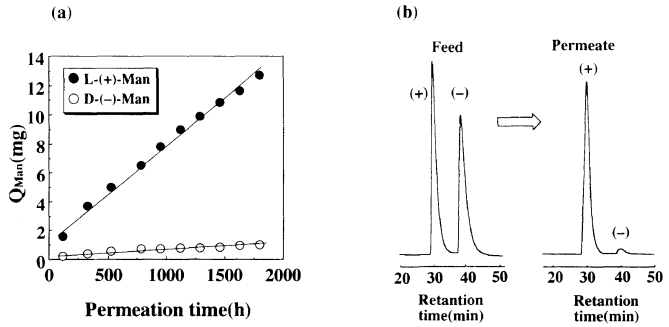


Figure 1. Enantioselective permeation of 1.0 wt% aq DL-(±)-mandelic acid solution through 10.7 wt% (−)-OMPS/PMMA membrane. (a) Plots of the quantity of permeated mandelic acid (Q_{Man}) *versus* permeation time. (b) HPLC chromatogram (column: Chiralpak WH) of the feed and the permeate.

mic bodies were conducted as follows: 0.5 g (−)-OMPS was added to 0.50 wt% aqueous solution of a racemic body and the mixture was stirred for 12 h. The (−)-OMPS containing the adsorbed compound was filtered and then washed with water for 4 h twice to extract the compound adsorbed on the (−)-OMPS. Adsorption quantity and enantioselectivity were determined by a method similar to the permeation described above.

Figure 1 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%e.e. The enantioselective permeation continued for more than 1797 h. The permeation rate (P) was 7.31×10^{-7} gmm^{-2}h^{-1}. The P was enhanced by applying pressure (5 kg·cm^{-2}) to 1.54×10^{-6} g·m·m^{-2}·h^{-1} although the %e.e. dropped to 32.9%e.e. (Figure 2). The enantioselective permeation was stable for 200 h, also.

The mechanism for the enantioselective permeation was discussed by examining the enantioselective adsorption of DL-Man and other racemic bodies to (−)-OMPS. Table II shows the enantioselectivities in the adsorption to (−)-OMPS and in the permeation through (−)-OMPS/PMMA. In all the three recemic bodies, (+)-isomers were selectively adsorbed

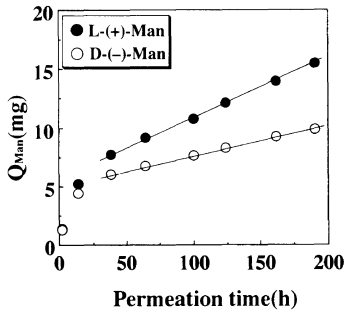


Figure 2. Enantioselective permeation of 0.10 wt% aq DL-(±)-mandelic acid solution through 11.4 wt% (−)-OMPS/PMMA membrane by applying 5 kg·cm^{-2}. Plots of the quantity of permeated mandelic acid (Q_{Man}) *versus* permeation time.

and predominantly permeated, that is, the isomers selected were identical in the adsorption and the permeation. Moreover, Man adsorbed in a high enantioselectivity permeated in a high enantioselectivity. These findings indicate that the enantioselectivity in the permeation was caused by the facilitated solution process at the membrane surface of (+)-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. As shown in Table III, (−)-OMPS/PDMS showed almost no enantioselectivity. Therefore, it was

Table II. Enantioselective adsorption of racemic bodies to (−)-OMPS

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

[a] Man = mandelic acid, Val = valine, and Phe = phenylalanine. [b] Pressure-driven permeation through 10—12 wt% OMPS/PMMA membrane.

Table III. Permeation[a] of DL-mandelic acid through (−)-OMPS/PMMA, (−)-OMPS/PDMS, and (+)-PDPSP/PMMA membranes

Binary blend membrane	P / $\times 10^{-6}$ g·m·m^{-2}·h^{-1}	%e.e.
10.7 wt% (−)-OMPS/PMMA	0.731	85.4
11.1 wt% (−)-OMPS/PDMS[b]	7.36	0.68
10.8 wt% (+)-PDPSP/PMMA[c]	1.17	1.72

[a] Concentration-driven permeation using 1.0 wt% aqueous feed solution. [b] PDMS, polydimethylsiloxane. [c] (+)-PDPSP, (+)-poly[1-{dimethyl(10-pinanyl)silyl}-1-propyne].

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.

In conclusion, (−)-OMPS/PMMA showed very high L-isomer selective permeability for DL-Man owing to the preferential adsorption of (−)-OMPS accumulated at the surface toward L-Man. Since only a few amount of the optically active compound was necessary in the membrane, it was very economical and practical. Further research into enantioselective permeation of other racemic bodies and that through other surface-modified membranes is now in progress.

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REFERENCES

1. M. Newcomb, R. C. Helogeson, and D. J. Cram, *J. Am. Chem. Soc.*, **96**, 7376 (1974).
2. A. Maruyama, N. Adachi, T. Takatsuki, M. Torii, K. Sanui, and N. Ogata, *Macromolecules*, **23**, 2748 (1990).
3. T. Aoki, K. Shinohara, and E. Oikawa, *Makromol. Chem., Rapid Commun.*, **13**, 565 (1992).
4. T. Aoki, S. Tomizawa, and E. Oikawa, *J. Membrane Sci.*, in press.
5. T. Aoki, E. Oikawa, Y. Hayakawa, and M. Nishida, *J. Membrane Sci.*, **57**, 207 (1991).
6. T. Aoki, Y. Toyoshima, T. Yoshizawa, and E. Oikawa, *Polymer*, **33**, 662 (1992).
7. T. Aoki, K. Yamagiwa, E. Yoshino, and E. Oikawa, *Polymer*, **34**, 1538 (1993).