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Optical resolution by vapour permeation of 1,3-butanediol and 2-butanol through (+)-poly{1-[dimethyl(10-pinanyl)silyl]-1-propyne} membrane

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Racemates of 1,3-butanediol, 2-butanol and their derivatives were enantioselectively separated by evapomeation (EV) and pervaporation (PV) through (+)-poly{1-[dimethyl(10-pinanyl)silyl]-1-propyne} membrane. The permeation rate (P, g m m^{-2} h^{-1}) and enantioselectivity (% enantiomeric excess (%ee) of the permeate) were very high. For example, the P and %ee values in EV for (±)-1,3-butanediol were 1.19×10^{-3} and 41.7%ee, and those in PV for (±)-2-butanol were 8.37×10^{-4} and 44.6%ee, respectively. This is the first example of vapour enantioselective permeation.

(Keywords: polymeric solid membrane; optical resolution; vapour permeation)

INTRODUCTION

Although high-performance liquid chromatography (h.p.l.c.) with a chiral stationary phase can efficiently separate various racemic mixtures, it can be used only for analysis and it is difficult for h.p.l.c. to separate a large quantity of racemates because of the many technical problems with its use on a large scale. 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. However, few optical resolution membranes have been reported[1-7], and their performance is not good in permeation rate, enantioselectivity, mechanical strength and durability. We have reported that a (+)-poly{1-[dimethyl(10-pinanyl)silyl]-1-propyne} [(+)-poly(DPSP), *Scheme 1*] membrane showed high enantioselectivity (the optical purity of the permeate = 86.1%ee where ee = enantiomeric excess) for aqueous solution of (±)-tryptophan in concentration-driven permeation[5]. However, the permeation rate (P, g m m^{-2} h^{-1}) was low (1.42×10^{-7}).

Optically active 1,3-butanediol (1,3-BD) and 2-butanol (2-BuOH) are very important as chiral synthons or starting materials in the fields of medicine, agricultural chemicals, and ferroelectric liquid crystals. However, it is difficult to obtain these optically active compounds directly from the corresponding racemates using h.p.l.c. with a chiral stationary phase because of the low interaction between the chiral stationary phase and the racemates whose structures are non-ionic and aliphatic.

In this paper, we report the first example of vapour enantioselective permeation, that is, evapomeation and pervaporation, of 1,3-BD and 2-BuOH, through the (+)-poly(DPSP) membrane with high permeation rate.

EXPERIMENTAL

Synthesis and membrane preparation

(+)-Poly(DPSP) was synthesized as reported previously[5]. The toluene solution of the polymer was cast on a polytetrafluoroethylene sheet, and the solvent was evaporated for 24 h. The resulting membrane was dried *in vacuo* for 24 h. Thickness (L) = 61.9–90.3 μm; area (A) = 3.14×10^{-4} m^2.

Evapomeation (EV)

Racemic 1,3-BD was supplied to the feed side of a glass cell, not in contact with the membrane. The feed side was evacuated and filled with the vapour of the racemate. The permeate side was connected to a cold trap in dry ice/methanol and evacuated at 2.0 mmHg. Evapomeation was carried out at ~30°C for 3.0–5.5 h (t). The permeate trapped was weighed (Q) and then the permeation rate (P, g m m^{-2} h^{-1}) was calculated from $P = (QL)/(At)$.

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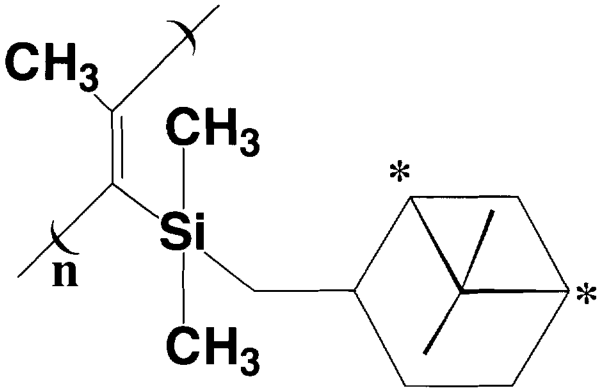


Scheme 1 Chemical structure of (+)-poly(DPSP)

Enantioselectivity in the permeation, i.e. optical purity of the permeate (%ee), was determined by the equation

$$\%\text{ee} = 100 \times (A_R - A_S)/(A_R + A_S)$$

The peak areas of (R)- and (S)-isomer (A_R and A_S) in the permeate were measured by h.p.l.c. with an optical resolution column (Chiralcell OB[R] manufactured by Daicel Chemical Co.) after acetylation of 1,3-BD permeated. Estimations for the other racemates were carried out in a similar manner.

Pervaporation (PV)

The feed side of a stainless steel cell was filled with 3.00 wt% methanol solution of racemic 1,3-BD. The permeate side was connected to a cold trap in dry ice/methanol and evacuated at 0.1 mmHg. Pervaporation was carried out for 5.0 h at 25°C. Estimations for the other racemates were conducted in a similar manner.

High-performance liquid chromatography

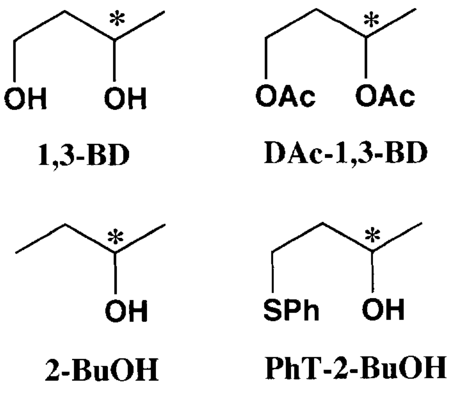
A silica gel surface was treated with diphenyldichlorosilane and then coated with (+)-poly(DPSP) by using tetrahydrofuran solution. The (+)-poly(DPSP)-coated silica gel thus obtained was slurry-packed in a stainless steel tube (25 × 0.46 cm i.d.)[8]. Distilled water was used as an eluent.

RESULTS AND DISCUSSION

Evapomeation (EV)

Figure 1 shows plots of quantity (Q) of (R)- and (S)-1,3-diacetoxybutane (DAc-1,3-BD) permeated through a (+)-poly(DPSP) membrane *versus* permeation time (t) when the racemic vapour was supplied. This membrane was permselective to (R)-DAc-1,3-BD. The %ee value of DAc-1,3-BD was enhanced to 30.4%ee in the permeate from 0%ee in the feed during the course of the permeation. The enantioselective permeation was stable and continued for more than 7 h. This is the first example of enantioselective EV. In addition, the permeation rate ($P = 4.17 \times 10^{-4}$) was ~3000 times higher than that in concentration-driven permeation of (±)-tryptophan through a (+)-poly(DPSP) membrane described in our previous paper[5].

Table 1 summarizes the results of enantioselective EV of the pure vapour of racemic 1,3-BD, DAc-1,3-BD, 2-BuOH and 4-phenylthio-2-butanol (PhT-2-BuOH) (*Scheme 2*) through the (+)-poly(DPSP) membrane. The membrane showed relatively high enantioselectivity for the pure vapour of 1,3-BD and DAc-1,3-BD (nos. 1 and 3). In particular, the P and %ee values for 1,3-BD were high at 100°C ($P = 1.19 \times 10^{-3}$, 41.7%ee, no. 1). The P value was ~8000 times higher than that of (±)-tryptophan in concentration-driven permeation described in our previous paper[5]. It is quite significant to enantioselectively separate racemic 1,3-BD through the solid membrane with a very high P value because of the difficulty in separating 1,3-BD by conventional methods such as h.p.l.c. with a chiral stationary phase. At room temperature, the enantioselectivity decreased to 5.5%ee (no. 2). This may be because the 1,3-BD molecules partly associated in the membrane at room temperature owing to the high polarity, and the associated molecules permeated. For the attainment of high enantioselectivity, therefore, it becomes necessary to suppress the self-association of the permeating molecules in the membrane by raising the temperature. On the other hand, DAc-1,3-BD, a derivative of 1,3-BD, was enantioselectively separated through the membrane, even at room temperature, with a relatively high optical purity of 30.4%ee (no. 3 and *Figure 1*). Since the degree of association of DAc-1,3-BD, which is less polar than 1,3-BD, is thought to be lower than that of 1,3-BD at room temperature, DAc-1,3-BD may be able to interact more effectively with the membrane polymer, and consequently yield a permeate of higher %ee value. EV of 2-BuOH gave a permeate with 9.3%ee when the



Scheme 2 Racemic mixtures used for enantioselective permeation experiment

Table 1 Enantioselective evapomeation through (+)-poly(DPSP) membrane ar room temperature

No.	Racemate[a]	$P \times 10^3$ (g m m^{-2} h^{-1})	%ee
1[b]	1,3-BD	1.19	41.7
2	1,3-BD	1.35	5.5
3	DAc-1,3-BD	0.417	30.4
4[c]	2-BuOH	0.424	9.3
5[d]	2-BuOH	4.03	2.7
6	PhT-2-BuOH	0.141	2.4

[a] See *Scheme 2*
[b] Temperature, 100 C
[c] Feed, 10 mmHg
[d] Feed, 35 mmHg

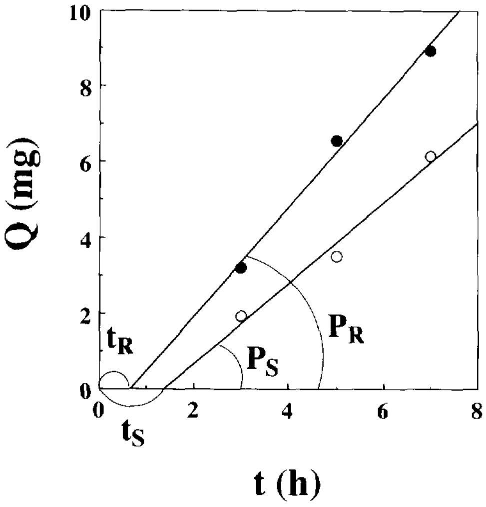


Figure 1 Plots of quantity (Q) of (R)- (●) and (S)-DAc-1,3-BD (○) permeated from a racemic mixture through (+)-poly(DPSP) membrane vs. permeation time (t) in evapomeation (EV)

Table 2 Enantioselective pervaporation through (+)-poly(DPSP) membrane

		Feed solution			
No.	Racemate	Concentration (wt%)	Solvent	$P \times 10^4$ (g m^{-2} h^{-1})	%ee
1	1,3-BD	3.00	methanol	2.25	88.7
2	2-BuOH	3.00	water	8.37	44.6

vapour pressure of the feed was 10 mmHg (no. 4). It is very interesting that the small-sized molecule was enantioselectively separated.

Since no enantioselective separation was observed using h.p.l.c. with a stationary phase prepared from (+)-poly(DPSP), the mechanism for enantioselective permeation for 1,3-BD and 2-BuOH was found to be unlike that for h.p.l.c. Separation was achieved by the accumulation of weak asymmetric interaction between racemates and the stationary phase. Moreover, as shown in *Figure 1*, the (R)-isomer had a higher permeation rate (P_R) and a shorter time lag (t_R), indicating higher diffusivity, than the (S)-isomer. Consequently, the enantioselective permeation was suggested to occur in the diffusion process. We assume at present that there were permeating paths with enantioselective recognition ability between the chiral pinanyl groups, which have a spatial arrangement in the membrane. EVs of 2-BuOH at a higher feed pressure (35 mmHg) and PhT-2-BuOH gave a permeate with very low %ee values (nos. 5 and 6). This may be because the permeating paths described above were deformed by 2-BuOH and PhT-2-BuOH, which have a high affinity for the membrane polymer.

In summary, it was found that the (+)-poly(DPSP) membrane can enantioselectively separate the vapour of racemates unless the permeating solutes associate with each other in the membrane and deform the permeating paths with enantioselective recognition ability by the solute. Since the two kinds of racemates with different properties (that is, highly polar 1,3-BD with no affinity for the polymer and less polar 2-BuOH with high affinity for the polymer) were enantioselectively separated through the membrane, it would be possible to separate other racemates by EV provided that the concentration of the solute in the membrane is quite low.

Pervaporation (PV)

Methanol solution of 1,3-BD (3.00 wt%) was enantioselectively separated by PV through the (+)-poly(DPSP) membrane. The optical purity was 88.7%ee, which was the best result in this paper (*Table 2*, no. 1). In addition, the P value was very high (2.25×10^{-4}) and ~1500 times higher than that of tryptophan in concentration-driven permeation described in our previous paper[5]. In the case of 1,3-BD, the %ee value in PV was higher than that in EV, but the P value in PV was lower than that in EV ($P = 1.19 \times 10^{-3}$, 41.7%ee). The higher %ee value in PV was probably caused by using a dilute solution, in which aggregation of 1,3-BD was suppressed.

Aqueous 2-BuOH solution (3.00 wt%) was also separated more efficiently compared with EV (44.6%ee, no. 2). 2-BuOH may be recognized more enantioselectively in PV than in EV. This is because the water solvent, which decreased the affinity of 2-BuOH for the membrane polymer, suppressed the deformation of the permeating paths with enantioselective recognition ability by 2-BuOH in the (+)-poly(DPSP) membrane.

In summary, 1,3-BD and 2-BuOH were more enantioselectively separated through (+)-poly(DPSP) membrane by PV with a high P value.

CONCLUSION

Racemic 1,3-BD and 2-BuOH were enantioselectively separated through (+)-poly(DPSP) membrane in EV and PV. The %ee of the permeate and P were very high. This is the first example of vapour enantioselective permeation. Further research into the detailed mechanism and the enantioselective recognition ability for other racemates of (+)-poly(DPSP) membrane are now in progress.

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