

# Polysulfones with Phenylalanine Derivatives as Chiral Selectors – Membranes for Chiral Separation

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**Abstract:** Polysulfone with a derivative of phenylalanyl residue as a chiral selector (PSf-Ac-D-Phe or PSf-Ac-L-Phe) were prepared by polymer reaction of benzylamine-modified polysulfones with N- $\alpha$ -acetyl-D-phenylalanine or N- $\alpha$ -acetyl-L-phenylalanine. Both polysulfones having a chiral selector gave durable self-standing membranes. The specific rotations of those polymers revealed that the chiral selectors were successfully introduced into the polysulfone. PSf-Ac-D-Phe membrane incorporated L-Glu in preference to D-Glu and *vice versa*. The chiral separation ability was studied by applying a concentration gradient as a driving force for membrane transport. Permselectivities for those two types of membrane reflected their adsorption selectivities. PSf-Ac-D-Phe membrane selectively transported L-Glu and *vice versa*. Predicted permselectivities by adopting membrane resistance coincided with the observed ones.

**Keywords:** Chiral separation, membrane, optical resolution, permselectivity, polysulfone.

## INTRODUCTION

Membrane separation is perceived to economically and ecologically competitive to other conventional separation methods since membrane separations, excepting pervaporation, are operated without phase transition. In addition to this, membrane separation is continuously operated under mild conditions. So far, membrane separation has been applied in various fields, such as water purification by reverse osmosis (RO), production of ultrapure water by nanofiltration (NF), waste water treatment by microfiltration (MF) or ultrafiltration (UF), concentration and recovery of valuable substrates by MF or UF, concentration or removal of charged materials by electrodialysis (ED), gas separation for recovery of H<sub>2</sub>, for concentration of O<sub>2</sub>, and for removal of CO<sub>2</sub>, hemodialysis, hemofiltration, and so forth. However, chiral separation has not been practically carried out by membrane separation technique. The demand for chiral separation by membrane has been required in industries, involving pharmaceuticals, agrochemicals, food additives, perfumes, and so forth. In chiral separation, excepting optical activity, the target enantiomer and the antipode show same physical and chemical properties under achiral environment [1-3]. From this, the existence of

chiral environment or chiral recognition site is requisite in membrane or membrane separation system so that chiral separation can be achieved by using membrane [4-7].

The authors' research group studied polymeric membranes having molecular recognition sites introduced by applying an alternative molecular imprinting [8-11] and those with chiral environment in a main chain [12, 13] or in a side chain [14] for chiral separation. As a side chain, alanyl derivatives were attached onto polysulfone *via* amide linkage. Among amino acids, there are 38 kinds of amino acid residue, which are expected to work as chiral environments or chiral selectors. In the present study, the authors focused their attentions on phenylalanine derivatives. Phenylalanine, containing benzyl moiety as a side chain of amino acid, was adopted as chiral selector in the present study. Phenylalanine has a larger and a more hydrophobic side chain, which might effectively exhibit chiral recognition ability, compared with alanine. To this end, N- $\alpha$ -acetyl-D-phenylalanine (Ac-D-Ala-OH) or N- $\alpha$ -acetyl-L-phenylalanine (Ac-L-Ala-OH) was adopted as a candidate for a chiral selector and each of those was introduced into polysulfone with benzylamine group (PSf-NH<sub>2</sub>) by polymer reaction. Chiral separation ability, such as adsorption selectivity and permselectivity, for those membranes were studied adopting racemic mixture of Glu as model racemates. In addition to these, a facile way to evaluate chiral separation ability of those membranes will be proposed

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by measuring membrane resistance of each enantiomer/membrane system.

## EXPERIMENTAL

### Materials

Polysulfone bearing benzylamine group (PSf-NH<sub>2</sub>) with a degree of substitution (DS) of 0.95 was prepared by the modification of polysulfone Udel P-3500 as reported previously [15]. Following similar procedures for the previous study [15], commercial polysulfone was lithiated with 1.0 mol equivalent of butyllithium, quenched with benzonitrile, then reduced with sodium borohydride to give PSf-NH<sub>2</sub> with DS of 0.95. N- $\alpha$ -Acetyl-D-phenylalanine (Ac-D-Phe-OH) and N- $\alpha$ -acetyl-L-phenylalanine (Ac-L-Phe-OH) were purchased from Watanabe Chemical Industries Ltd. (Hiroshima, Japan) and used without purification. N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (WSCD/HCl) and 1-hydroxybenzotriazole (HOBt) were purchased from Peptide Institute Inc. (Osaka, Japan) and used without further purification. N,N-Dimethylformamide (DMF) was purified by conventional method [16]. Ethanol, dimethylsulfoxide (DMSO), D-glutamic acid (D-GLu), and L-glutamic acid (L-GLu) were obtained from commercial sources and used as received. Water purified with an ultrapure water system (Simpli Lab. Millipore S. A., Molsheim, France) was used.

### Synthesis of the Membrane Materials

As shown in Figure 1, a 15.0 cm<sup>3</sup> DMF solution containing requisite amounts of PSf-NH<sub>2</sub>, Ac-Phe-OH (Ac-D-Phe-OH or Ac-L-Phe-OH), WSCD/HCl, and HOBt was stirred at 40 °C for 2 weeks. After the reaction, the reaction mixture was poured into ethanol and the prescribed product was washed with ethanol and dried *in vacuo*. A 1.15 g (96.6 %) of the modified polysulfone with Ac-D-Phe as a chiral selector, PSf-Ac-D-Phe, was

obtained, while the yield of PSf-Ac-L-Phe was 1.18 g (98.3 %).

### Characterization of Membrane Materials

The Fourier-transform infrared (FTIR) spectra of DMSO-cast membranes were recorded by using Perkin-Elmer Spectrum GX; 64 scans at a resolution of 4 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra (300 MHz) were recorded in DMSO-d<sub>6</sub> using a BRUKER AV-300 and the solvent signal (2.50 ppm [17]) was as an internal standard.

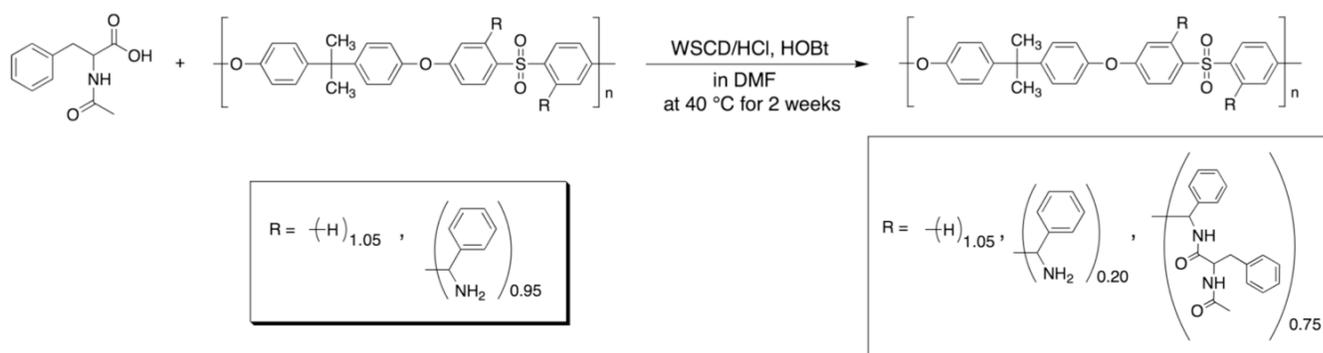
The thermal stability of the modified polymer was evaluated on a Hi-Res Modulated TGA 2950 (TA instruments) under nitrogen at a heating rate of 5.0 °C min<sup>-1</sup>.

Dynamic mechanical thermal analysis (DMTA) measurement was carried out with a dynamic analyzer, RSA III (TA Instruments, Inc.) in tension mode. The experiment was performed at a frequency of 1 Hz and a heating rate of 2.0 °C min<sup>-1</sup> from 80 °C to 140 °C for PSf-Ac-D-Phe and from 80 °C to 120 °C for PSf-Ac-L-Phe. The dimension of sample was 20.01 x 6.00 x 0.11 mm<sup>3</sup>.

The specific rotations were obtained with Horiba SEPA-200 Polarimeter at 589 nm at ambient temperature in DMF.

### Membrane Preparation

A 0.30 g of polymer was dissolved in 3.0 cm<sup>3</sup> of DMF. The polymer solution was poured into a flat laboratory dish (11.6 cm diameter) and the solvent was allowed to be evaporated at 50 °C for 2 d. The thickness of PSf-Ac-D-Phe membrane determined by micrometer was 48  $\mu$ m and that of PSf-Ac-L-Phe one being 40  $\mu$ m.



**Figure 1:** Synthetic scheme of polysulfones with phenylalanyl residue as a chiral selector.

## Adsorption Selectivity

The membranes were immersed in an aqueous solution of racemic Glu (each enantiomeric Glu was  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ), and the membranes were allowed to be equilibrated at  $40^\circ\text{C}$ . A 0.02 wt.-% of sodium azide was added as a fungicide. Aliquots of the solution at the initial stage and after equilibrium had been reached were used for quantitative estimation by liquid chromatography (LC) [Jasco PU1580, equipped with a UV detector (Jasco UV1570)] employing Chiralpak MA(+) column [50 x 4.6 (i.d.), Daicel Chemical Ind.]. An aqueous copper sulfate solution was used as a mobile phase.

The amount of Glu in the supernatant subtracted from the initial amount in the solution gave the amount of Glu adsorbed by the membrane. The adsorption selectivity  $S_{A(i/j)}$  is defined as:

$$S_{A(i/j)} = ((i\text{-Glu})/(j\text{-Glu})) / ([i\text{-Glu}]/[j\text{-Glu}]) \quad (1)$$

where (i-Glu) and [i-Glu] are the amount of Glu adsorbed in the membrane and the concentration in the solution after equilibrium had been reached. Hereafter, subscripts of D and L mean the D- and the L-isomer, respectively.

## Enantioselective Transport

A membrane ( $3.0 \text{ cm}^2$ ) was fixed tightly with Parafilm between two chambers of a permeation cell. The volume of each chamber was  $40.0 \text{ cm}^3$ . An aqueous solution of racemic Glu was placed in the left-side chamber (L-side) and an aqueous solution in the right-side chamber (R-side). Each concentration of racemic Glu was fixed to be  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ . In both chambers, 0.02 wt.-% of sodium azide was added as a fungicide. All experiments were carried out at  $40^\circ\text{C}$  with stirring. An aliquot was drawn from the permeate side (R-side) at each sampling time. The amounts of D- and L-isomers that transported through the membrane were determined by LC as described above.

The flux,  $J$  ( $\text{mol cm}^{-2} \text{ h}^{-1}$ ), is defined as:

$$J = Q/At \quad (2)$$

where  $Q$  (mol) is the amount of transported Glu,  $A$  ( $\text{cm}^2$ ) the effective membrane area, and  $t$  (h) is the time.

The permselectivity  $\alpha_{i/j}$  is defined as the flux ratio  $J_i/J_j$  divided by the concentration ratio [i-Glu]/[j-Glu]

$$\alpha_{i/j} = (J_i/J_j) / ([i\text{-Glu}]/[j\text{-Glu}]) \quad (3)$$

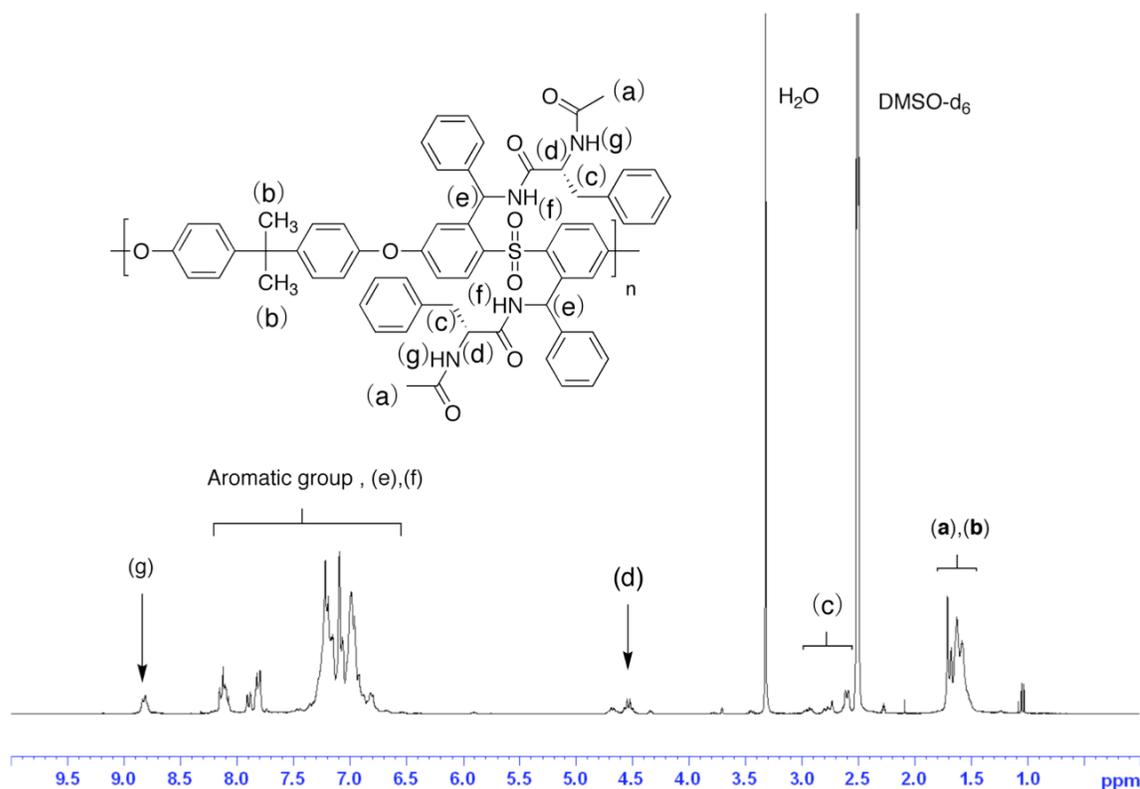


Figure 2:  $^1\text{H}$  NMR spectrum of PSf-Ac-D-Phe. (300 MHz;  $\text{DMSO-d}_6$ ).

**Table 1: Results for Introduction of Chiral Selector onto Polysulfone**

	PSf-NH <sub>2</sub> g (mol)	Ac-D-Phe-OH g (mol)	Ac-L-Phe-OH g (mol)	WSCD/HCl g (mol)	HOBt g (mol)	Yield g (%)	DS <sup>a</sup> (%) <sup>b</sup>
PSf-Ac-D-Phe	1.02 (1.89×10 <sup>-3</sup> ) <sup>c</sup>	1.09 (5.26×10 <sup>-3</sup> )	- (-)	1.09 (5.68×10 <sup>-3</sup> )	0.77 (5.70×10 <sup>-3</sup> )	1.15 (96.6)	0.75 (79.0)
PSf-Ac-L-Phe	1.03 (1.90×10 <sup>-3</sup> ) <sup>c</sup>	- (-)	1.19 (5.74×10 <sup>-3</sup> )	1.10 (5.74×10 <sup>-3</sup> )	0.78 (5.77×10 <sup>-3</sup> )	1.18 (98.3)	0.75 (79.0)

<sup>a</sup>Degree of substitution.<sup>b</sup>(DS/0.95) × 100.<sup>c</sup>Mole number of constitutional repeating unit (CRU) of PSf-NH<sub>2</sub>.

### Membrane Conductance (Membrane Resistance)

Membrane conductance was estimated from membrane resistance. The resistances of each D-Glu or L-Glu solution with membrane and without membrane were measured by using Portable Kohlrausch Bridge TYPE BF-62A (Shimadzu Rika Instruments Co., Ltd.) and CO-1305 oscilloscope (KENWOOD). The area of each platinum electrode was 1.0 cm<sup>2</sup> and the distance between the electrodes was fixed to be 7.0 cm. An aqueous solution of optically pure D-Glu or L-Glu, of which concentration being 1.0 × 10<sup>-3</sup> mol dm<sup>-3</sup>, was poured into both chambers (R-side and L-side). The resistance was measured at a constant temperature of 40 °C with stirring. The measurement of resistance was completed within a few minutes.

## RESULTS AND DISCUSSION

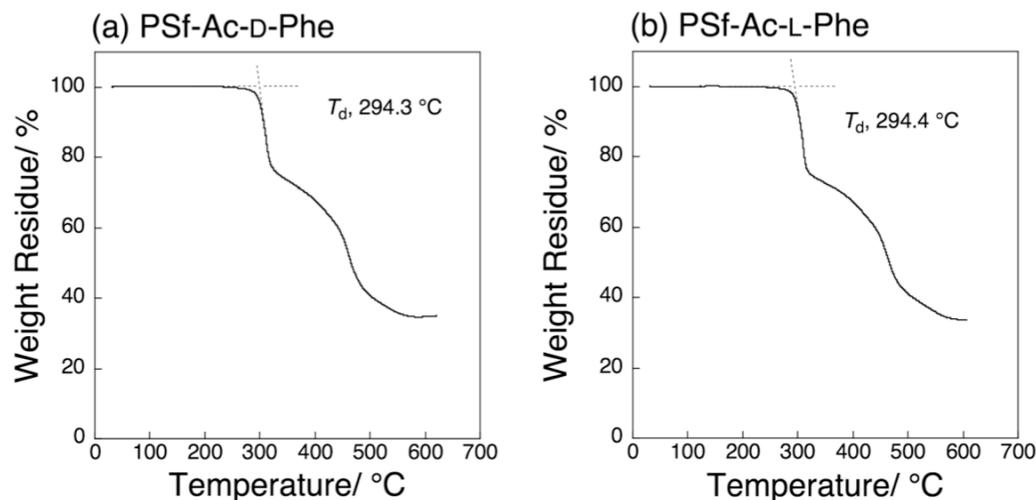
### Polysulfones with Phenylalanine Derivative

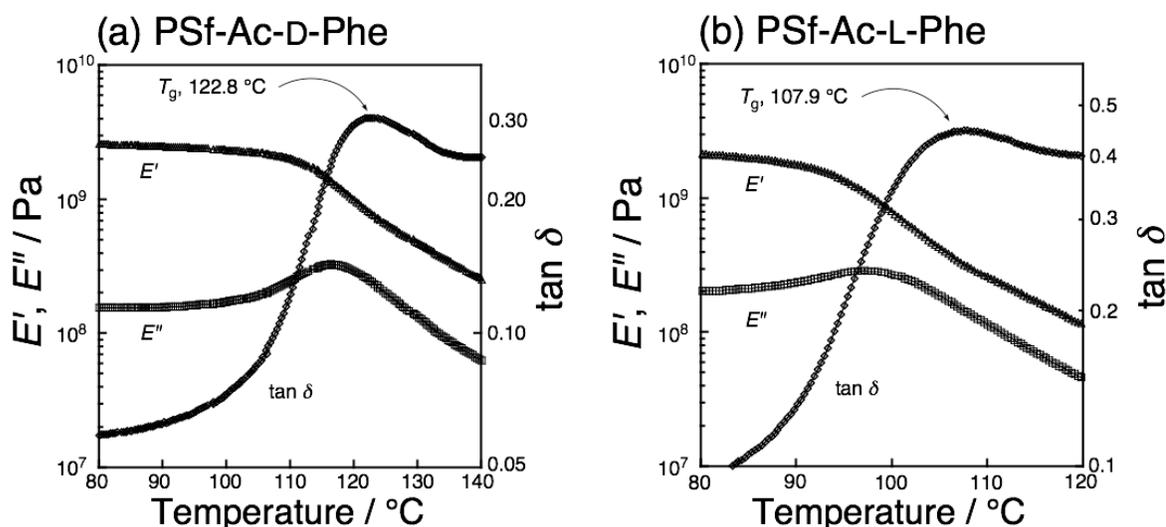
In the IR spectra, the amide I bands were observed at 1656 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of PSf-Ac-D-Phe

is shown in Figure 2, which was similar to the one observed for PSf-Ac-L-Phe. From <sup>1</sup>H NMR spectra, 79.0 % of PSf-NH<sub>2</sub> amino groups were concluded to have reacted with both Ac-D-Phe-OH and Ac-L-Phe-OH by using the area of amide proton (g) and methyl proton (a) and (b). From above, the degree of substitution (DS) for the phenylalanine moiety in both PSf-Ac-D-Phe and PSf-Ac-L-Phe was determined to be 0.75. The results are summarized in Table 1 together with reaction conditions.

### Thermal Properties

Figure 3 shows thermogravimetric analysis (TGA) thermographs for PSf-Ac-D-Phe and PSf-Ac-L-Phe. Comparing with thermal stabilities of analogous polymers, PSf-Ac-Ala's [18], which had N- $\alpha$ -acetylalanine derivative instead of Ac-Phe as a chiral selector, the degradation temperature,  $T_d$ , for the present polymers were slightly lower than that for PSf-Ac-Ala ( $T_d$  for PSf-Ac-D-Ala, 306 °C;  $T_d$  for PSf-Ac-L-Ala, 307 °C [18]). This led to the conclusion that the side group of Phe residue was more flexible than that

**Figure 3:** TGA curves of PSf-Ac-D-Phe (a) and PSf-Ac-L-Phe (b). (Heating rate, 5.0 °C min<sup>-1</sup>).



**Figure 4:** Temperature dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  for PSf-Ac-D-Phe (a) and PSf-Ac-L-Phe (b) at a frequency of 1 Hz and a heating rate of  $2.0^\circ\text{C min}^{-1}$ .

in Ala residue in the present study. This conclusion will be closely correlated to the following glass transition temperature.

Figure 4 shows the dependence of dynamic storage modulus  $E'$ , dynamic loss modulus  $E''$ , and  $\tan \delta$  on temperature for those two types of polymer. The peak on  $\tan \delta$ , assigned to the glass transition temperature  $T_g$ , can be found at  $122.8^\circ\text{C}$  for PSf-Ac-D-Phe and  $107.9^\circ\text{C}$  for PSf-Ac-L-Phe, respectively. The  $T_g$ 's for PSf-Ac-Ala's were higher than those for PSf-Ac-Phe's and over  $190^\circ\text{C}$  [18].  $T_g$ 's were observed to decrease with the enlargement of side group of amino acid residue. In the present study,  $T_g$  values are more dependent on the flexibility, rather than the size of the amino acid residue, which causes steric hindrance [19]. Even though two types of PSf-Ac-Phe polymer have similar DS of 0.75, PSf-Ac-D-Phe gave around  $15^\circ\text{C}$  higher  $T_g$  than PSf-Ac-L-Phe. The micro structure of the polymer, in other words, the way of attachment of Phe moiety *via* amide linkage for the former and that for the latter might be a little bit different, though, at the moment, there are no definite experimental results to explain the difference in observed  $T_g$ .

### Chiroptical Properties

The optical rotations ( $[\alpha]_D$ ) of the polysulfone with chiral selector Phe are summarized in Table 2 together with those for the starting chiral building blocks. The optical rotations for PSf-Ac-D-Phe were opposite to that for PSf-Ac-L-Phe. The results in Table 2 revealed that optically active polymers were successfully obtained *via* polymer reaction between PSf-NH<sub>2</sub> and phenylalanine derivative.

**Table 2: Specific Rotations of PSf-Ac-Phe and their Chiral Building Blocks**

	$[\alpha]_D^*$
	$\text{deg cm}^2 \text{g}^{-1}$
PSf-Ac-D-Phe	-0.54
PSf-Ac-L-Phe	0.49
Ac-D-Phe-OH	-3.80
Ac-L-Phe-OH	3.75

\*In DMF;  $c = 1.0 \text{ g dL}^{-1}$ ;  $L = 10 \text{ cm}$ .

### Adsorption Selectivity

Adsorption selectivity of the present membranes toward racemic mixture of Glu was studied. The results of adsorption study are summarized in Table 3. PSf-Ac-D-Phe membrane adsorbed L-Glu in preference to the D-isomer of Glu and *vice versa*. The adsorption selectivity of PSf-Ac-D-Phe membrane toward L-Glu was determined to be 1.39, while that of PSf-Ac-L-Phe one toward the D-isomer to be 1.33. In the previous study, PSf-Ac-Ala membranes showed opposite adsorption selectivity [14,18]. This might be due to the difference in amino acid residue attached as a chiral selector. From above results, those membranes can be expected to exhibit chiral separation ability of racemic mixture, which will be confirmed in the next section.

### Chiral Separation

Chiral separation ability of the present membranes was studied by adopting racemic mixture of Glu as model racemates. In the present study, concentration gradient was adopted as a driving force for membrane transport. Time-transport curves of racemic mixture of

Table 3: Adsorption Selectivity of PSf-Ac-Phe Membranes

Membrane	D-Glu		L-Glu		$S_{A(D/L)}$	$S_{A(L/D)}$
	(D-Glu)/mem.	(D-Glu)/(CRU)*	(L-Glu)/mem.	(L-Glu)/(CRU)*		
	mol/g-mem.		mol/g-mem.			
PSf-Ac-D-Phe	$3.44 \times 10^{-6}$	$2.30 \times 10^{-3}$	$4.78 \times 10^{-6}$	$3.20 \times 10^{-3}$	0.72	1.39
PSf-Ac-L-Phe	$4.93 \times 10^{-7}$	$3.29 \times 10^{-4}$	$3.69 \times 10^{-7}$	$2.47 \times 10^{-4}$	1.33	0.75

\*Mole number for constitutional repeating unit (CRU) of PSf-Ac-Phe.

Glu through those membranes are shown in Figure 5. As can be seen, permselectivities for those membranes toward racemic mixture of Glu reflected their adsorption selectivities. In other words, PSf-Ac-D-Phe membrane selectively transported L-Glu, which was preferentially incorporated into it, and *vice versa*.

From the steady-state part of time-transport curves, both fluxes, which were adopted to determine permselectivity as described above, and apparent time-lag can be determined. Following solution-diffusion model [20,21], diffusivity selectivity, which is a ratio of diffusion coefficients of *i*- and *j*-isomer,  $S_{D(i/j)} (= D_i/D_j; D_i$  and  $D_j$  are the diffusion coefficients of *i*- and *j*-isomer, respectively), can be determined by equation (4), using permselectivity and adsorption selectivity.

$$S_{D(i/j)} = \alpha_{ij}/S_{A(i/j)} \quad (4)$$

Apparent diffusivity selectivity can be also determined by equation (5), using apparent time-lag.

$$S_{D(i/j)} = \theta_j/\theta_i \quad (5)$$

where  $\theta_i$  and  $\theta_j$  are the apparent time lag of *i*- and *j*-isomer, respectively. Diffusivity selectivities determined

by both methods are summarized in Table 4. As can be seen, diffusivity selectivity determined by permselectivity and adsorption selectivity coincides with apparent diffusivity selectivity estimated by time-lag data.

In the present study, diffusivity selectivity is preferable to less adsorbed enantiomer as often observed in chiral separation [8,11,13,22-27]. The diffusion of enantiomer selectively adsorbed into the membrane was retarded by a relatively strong interaction between the enantiomer and the membrane. As a result, the antipode was diffused within the membrane faster than the enantiomer preferentially incorporated into the membrane. If the interaction between the enantiomer selectively adsorbed and the membrane was strong, permselectivity would be hardly expressed or the corresponding antipode would be selectively transported.

#### Prediction of Permselectivity by Membrane Resistance

As can be seen in Figure 5, in general, it takes a long time to study membrane transport phenomena. In

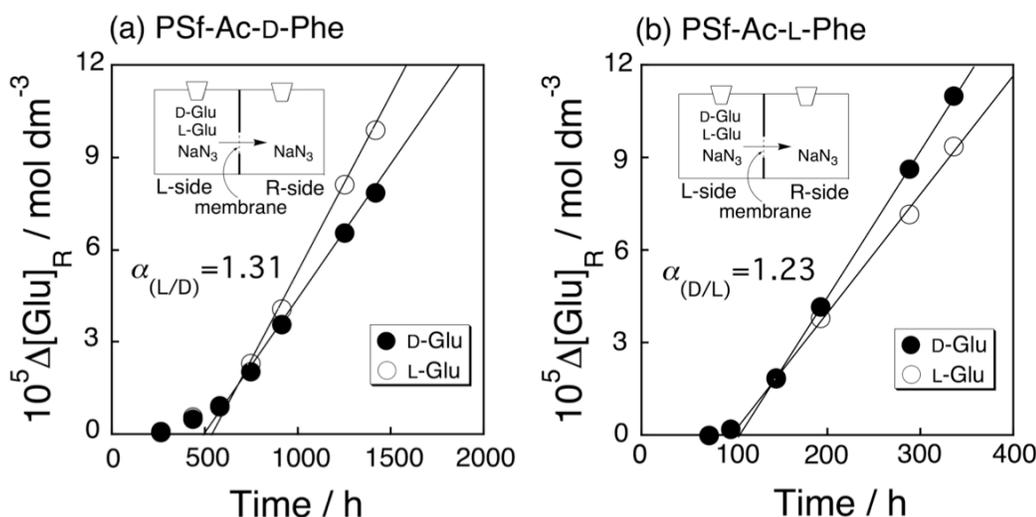


Figure 5: Time-transport curves of racemic mixture of Glu through PSf-Ac-D-Phe (a) and PSf-Ac-L-Phe (b) membranes at 40 °C adopting a concentration gradient as a driving force for membrane transport.

**Table 4: Summary of Membrane Transport**

Membrane	$\theta_b/h$	$\theta_l/h$	$\theta_l/\theta_b (= S_{D(D/L)})^a$	$\theta_b/\theta_l (= S_{D(L/D)})^a$	$S_{D(D/L)}^b$	$S_{D(L/D)}^c$
PSf-Ac-D-Phe	506	547	1.08	0.93	1.06	0.94
PSf-Ac-L-Phe	105	95	0.90	1.11	0.92	1.09

<sup>a</sup>Determined from time lag.

<sup>b</sup>Determined from permselectivity and adsorption selectivity;  $S_{D(D/L)} = \alpha_{D/L}/S_{A(D/L)}$ .

<sup>c</sup>Determined from permselectivity and adsorption selectivity;  $S_{D(L/D)} = \alpha_{L/D}/S_{A(L/D)}$ .

**Table 5: Conductance and Membrane Performance**

	$10^{-3} R_D/\Omega$	$10^{-3} R_L/\Omega$	$G_D/G_L^a$	$G_L/G_D^b$	$\alpha_{D/L}$	$\alpha_{L/D}$
PSf-Ac-D-Phe	3.80	2.90	0.76	1.31	0.76	1.31
PSf-Ac-L-Phe	5.53	6.79	1.23	0.81	1.23	0.81

<sup>a</sup> $G_D/G_L = R_L/R_D$ .

<sup>b</sup> $G_L/G_D = R_D/R_L$ .

the previous study [28], the authors' research group proposed that it was possible to predict the permselectivity of racemic mixture through a given membrane by measurements of membrane resistance for each enantiomer. The observed resistance ( $R_{obs,i}$ ) consists of that for solution ( $R_{s,i}$ ) and that for membrane ( $R_{m,i}$ ). The membrane resistances for each Glu for a given membrane were determined by the following equation:

$$R_{m,i} = R_{obs,i} - R_{s,i} \quad (6)$$

The determined membrane resistances for each enantiomer for each membrane are summarized in Table 5. The reciprocal of the membrane resistance is referred to as the membrane conductance. The ratio of the membrane conductance thus determined for each enantiomer will reflect permselectivity. The predicted permselectivity will be determined by the following equation:

$$\alpha_{ij} = G_{m,i}/G_{m,j} = (1/R_{m,i})/(1/R_{m,j}) = R_{m,j}/R_{m,i} \quad (7)$$

where  $G_{m,i}$  means the membrane conductance for the enantiomer  $i$ -Glu and  $R_{m,i}$  is the membrane resistance for  $i$ -Glu. The conductance ratios thus calculated and observed permselectivities are also given in Table 5 together with membrane resistances. From Table 5, as proposed in the previous study [28], the measurement of membrane resistance is a facile way to predict chiral separation ability.

In the present study, the membrane resistance was measured at one fixed concentration of  $1.0 \times 10^{-3}$  mol  $\text{dm}^{-3}$ , at which the performances for two types of membrane were studied. Concentrations of enantiomer, which were in contact with the membrane,

had been changed, the transport mechanism, in some case, would have been deduced.

## CONCLUSIONS

Polysulfone with a derivative of phenylalanyl residue as a chiral selector (PSf-Ac-D-Phe or PSf-Ac-L-Phe) were prepared by polymer reaction of benzylamine-modified polysulfones with  $N$ - $\alpha$ -acetyl-D-phenylalanine or  $N$ - $\alpha$ -acetyl-L-phenylalanine. The specific rotations of those polymers revealed that the chiral selectors were successfully introduced into the polysulfone. Both polysulfones having a chiral selector gave durable self-standing membranes. PSf-Ac-D-Phe membrane incorporated L-Glu in preference to D-Glu and *vice versa*. The chiral separation ability was studied by applying a concentration gradient as a driving force for membrane transport. Permselectivities for those two types of membrane reflected their adsorption selectivities. PSf-Ac-D-Phe membrane selectively transported L-Glu and *vice versa*. The permselectivity of PSf-Ac-D-Phe membrane toward the L-Glu was determined to be 1.31 and that of PSf-Ac-L-Phe one to be 1.23. Predicted permselectivities by adopting membrane resistance coincided with the observed ones.

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