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Optical Resolution Membranes from Polysulfone Bearing Alanine Derivative as a Chiral Selector

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Polysulfones bearing a derivative of alanyl residue employed as a chiral selector were prepared by polymer modification. The specific rotation ($[\alpha]_D$) of the polysulfone with a derivative of D-alanyl residue (PSf-Ac-D-Ala) was determined to be 2.87 deg cm^2 g^{-1} (c = 1.00 g/dL in DMF) and that with L-alanyl residue (PSf-Ac-L-Ala) to be -2.36 deg cm^2 g^{-1} (c = 1.00 g/dL in DMF), implying that the chiral selector of D-alanyl or L-alanyl residue was successfully introduced into the polysulfone. Those two types of modified polysulfone gave durable self-standing membranes. The membrane from PSf-Ac-D-Ala preferentially adsorbed the D-isomer of Glu from racemic mixture of Glu and *vice versa*; that is, L-Glu was selectively incorporated into PSf-Ac-L-Ala membrane. Chiral separation ability was studied by applying a potential difference as a driving force for membrane transport. The membrane performance was greatly dependent on the applied potential difference. At an applied potential difference of 18.0 V, the permselectivities for those membranes reflected their adsorption selectivity, in other words, the permselectivity of PSf-Ac-D-Ala toward D-Glu ($\alpha_{D/L}$) was determined to be 1.40, and that of PSf-Ac-L-Ala toward the L-isomer ($\alpha_{L/D}$) to be 1.48.

Introduction

Chirality plays a crucially important role in biological processes.[1,2] For instance, drug enantiomers with different chiral environments often show pharmacological activities dependent on absolute configuration. In view of this, the production of enantiomerically pure compounds has gained increasing attention in industries involving pharmaceuticals, agrochemicals, fragrances, food additives, and so forth. Asymmetric synthesis is perhaps one of the ultimate methods to obtain enantiomerically pure compounds. Although asymmetric synthesis has been intensively studied, [3-7] its development is still slow. Optical resolution of racemates is an alternative way to obtain optically pure compounds. The various methods to achieve optical resolution include crystallization resolution, kinetic resolution, chromatographic separation, and membrane-based separation. Membrane chiral separation is regarded as a promising and potentially convenient method to obtain enantiomerically pure compounds,[8-11] since it can be operated continuously under mild conditions and could be ecologically and economically competitive with other processes.

Membrane-based chiral separation processes have been studied in the form of liquid membranes[12-16] or polymeric membranes, [17-35] with the latter method being the focus of the authors' research. Polymeric membranes having molecular recognition sites introduced by applying an alternative molecular imprinting[22,26,35] or polymer reaction[30,32] and those with chiral environments[33,34] were used as materials for chiral separation membranes. Modified polysulfone membranes for chiral separations, [22,30,32] pervaporation separation[36-38] and selective separation of CO_2[39] have been investigated by the authors. In the present study, polysulfone containing benzylamine group (PSf-NH_2),[40] which had previously been used as a precursor for molecular recognition materials,[41] was adopted as a reactive base material for introducing D- and L-alanine derivatives (N-α-acetyl-D-alanine and N-α-acetyl-L-alanine), and the chiral separation ability of those membranes was investigated.

Experimetal Part

Materials

PSf-NH_2 with a degree of substitution (DS) of 1.50 was prepared by the modification of polysulfone Udel P-3500 as reported previously.[40] Following similar procedures for the previous study, [40] commercial polysulfone was lithiated with 2.0 mol equivalents of *n*-butyllithium, quenched with benzonitrile, then reduced with sodium borohydride to

give PSf-NH_2 with DS of 1.50. N-α-Acetyl-D-alanine (Ac-D-Ala-OH), N-α-acetyl-L-alanine (Ac-L-Ala-OH), dicyclohexylcarbodiimide (DCC), D-glutamic acid (D-Glu), L-glutamic acid (L-Glu), ethanol, methanol, and dimethylsulfoxide (DMSO) were used without purification. N,N-Dimethylfomamide (DMF) was purified by the conventional method.[42] Deionized water was obtained 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 10.0 cm^3 DMF solution containing requisite amounts of PSf-NH_2, Ac-Ala-OH (Ac-D-Ala-OH or Ac-L-Ala-OH), and DCC was stirred at the prescribed temperature for 2 weeks. In the introduction of Ac-D-Ala into PSf-HH_2, the polymer reaction was done at 25 °C. As for the introduction of Ac-L-Ala into PSf-NH_2, the polymer reaction was done at ambient temperature. After the reaction, the reaction mixture was poured into ethanol and the prescribed product was washed with ethanol and dried in *vacuo*. 1.07 g (83.5 %) of the modified polysulfone with Ac-D-Ala as a chiral selector, PSf-Ac-D-Ala, was obtained, while the yield of PSf-Ac-L-Ala was 0.83 g (64.8 %).

Characterization of the Membrane Materials

The FTIR spectra of DMSO-cast membranes were recorded by using Perkin-Elmer Spectrum GX; 64 scans at a resolution of 4 cm^{-1}. The ^1H NMR spectra (300 MHz) were recorded in DMSO-d_6 using a BRUKER AV-300 and the solvent signal (2.50 ppm[43]) was as an internal standard. Differential scanning calorimetry (DSC) measurements were performed with a Shimadzu DSC-60 at a heating rate of 10 °C min^{-1} and a nitrogen flow rate of 50 cm^3 min^{-1}. 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 20 °C min^{-1}. 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^3 of DMF. The polymer solution was poured into a flat laboratory dish (11.6 cm diameter) and the solvent was allowed to evaporate at 50 °C for 2 days. The thickness of the membrane thus obtained was

around 23 - 25 μm.

Adsorption of Racemic Mixtures to the Membranes

The membranes were immersed in a 50 vol% aqueous ethanol solution of racemic Glu, (concentration of each enantiomeric Glu was 2.0×10^{-4} mol dm^{-3}), and the membranes were allowed to equilibrate at 40 °C. Aliquots of the solution at the initial stage and after equilibrium had been reached were used for quantitative estimation by liquid chromatography (LC) [JASCO PU 1580, equipped with a UV detector (JASCO UV 1570)] employing CHIRALPAK MA(+) column [50 × 4.6 mm (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:

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

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. The subscripts D and L refer to the D-isomer of Glu and the L-isomer of Glu, respectively.

Enantioselctive Electrodialysis

A membrane (area, 3.0 cm^2) was fixed tightly with Parafilm between two chambers of a permeation cell. Each 40.0 cm^3 chamber was filled with 50 vol% aqueous ethanol solution of a racemic mixture of Glu, each enantiomer having a concentration of 2.0×10^{-4} mol dm^{-3}. The electrodialysis was carried out with a prescribed applied potential difference between platinum electrodes (1.0 cm^2; distance between the electrodes, 70 mm) at 40 °C with stirring. The amounts of D- and L-Glu that were transported through the membrane were determined by LC as described above.

The flux J (mol cm^{-2} h^{-1}) is defined as follows:

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

where Q (mol) is the amount of transported Glu, A (cm^2) is 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]):

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

Results and Discussion

Syntheses of Polysulfones with Alanine Derivative

In the IR spectra, the amide I bands were observed at 1655 cm^{-1}. ^1H NMR spectrum of PSf-Ac-D-Ala is shown in Figure 2, which was similar to the one observed for PSf-L-Ala. From ^1H NMR spectra, it was calculated that 74.7 % of PSf-NH_2 amino groups reacted with Ac-D-Ala-OH and 84.0 % reacted with Ac-L-Ala-OH. From above, the degree of substitution (DS) for alanyl moiety in PSf-Ac-D-Ala was determined to be 1.12, and that in PSf-L-Ala to be 1.26. The results are summarized in Table 1.

Thermal Properties

Figure 3 shows thermogravimetric analysis (TGA) thermographs for PSf-Ac-D-Ala and PSf-Ac-L-Ala. Thermal stability is moderate, which is due to the fact that the amino group in the alanyl residue is protected by the acetyl (Ac) group. The weight loss was observed above the temperature of 200 °C and the glass transition temperature T_g, which could be observed at around 200 °C,[40] was not prominent because the T_g endotherm overlapped with the degradation point.

Chiroptical Properties

The optical rotations ($[\alpha]_D$) of the polysulfone chiral membranes are summarized in Table 2, together with those of the Ac-Ala-OH. The optical rotation for PSf-Ac-D-Ala was opposite to that of PSf-Ac-L-Ala. The results in the table revealed that optically active polysulfones were successfully obtained *via* polymer reaction between PSf-NH_2 and Ac-Ala-OH.

Adsorption Selectivity

The results of the adsorption study are summarized in Table 3. PSf-Ac-D-Ala adsorbed the D-isomer of Glu in preference to the corresponding L-isomer and *vice versa*. The adsorption selectivity of PSf-Ac-D-Ala toward D-Glu, $S_{A(D/L)}$, was determined to be 1.90, while $S_{A(L/D)}$ for PSf-Ac-L-Ala was to be 2.00. From those results, it can be expected that the present polysulfones with a chiral selector showed enantioselective separation ability of racemates, which is confirmed in the next section.

Enantioselective Electrodialysis

Initially, the chiral separation ability of the two types of membrane was studied by using a concentration gradient as a driving force for membrane transport. The concentration difference between the feed side and the permeate side for each enantiomer was fixed at 2.0×10^{-4} mol dm^{-3}. However, the flux values of the racemic mixture of Glu were too low to be precisely determined. From this, a potential difference was adopted as a driving force for membrane transport. Figure 4 shows time-transport curves of a racemic mixture of Glu through the two types of membrane at the potential difference of 18.0 V. As can be seen, D-Glu, which was preferentially incorporated into PSf-Ac-D-Ala membrane, was selectively transported through PSf-Ac-D-Ala membrane and *vice versa*. The permselectivity of PSf-Ac-D-Ala membrane toward D-Glu was determined to be 1.40 and that of PSf-Ac-L-Ala one toward L-Glu to be 1.48, which was close to its adsorption selectivity.

In membrane transport, it was often observed that the transport of a preferentially incorporated enantiomer is retarded by a relatively strong interaction between the enantiomer and the membrane, and as a result the antipode is preferentially transported through the membrane.[18-21,26] From the above, the membrane performance was expected to be greatly dependent on the applied potential difference, as observed previously.[26] Thus, membrane performance was investigated at potential differences of 6.0 V, 12.0 V and 18.0 V and the results are summarized in Figure 5. In the figure, the permselectivity and the total flux for both membranes are plotted as a function of the applied potential difference. The flux increased linearly with the increase in the potential difference, passing through the origin. As expected, in both membranes, the permselectivity decreased with the decrease in the applied potential difference. Both membranes showed a permselectivity of around 0.88 at the applied potential difference

of 12.0 V and then the opposite permselectivity was observed at 6.0 V; in other words, PSf-Ac-D-Ala membrane transported the L-isomer of Glu in preference to the corresponding D-isomer and *vice versa*. The permselectivity of PSf-Ac-D-Ala membrane at 6.0 V, $\alpha_{D/L}$, was determined to be 0.60 and that of PSf-Ac-L-Ala one, $\alpha_{L/D}$, to be 0.47.

The driving force for the membrane transport by the concentration gradient of 2.0 x 10^{-4} mol dm^{-3} corresponded to that by an applied potential difference of 0.27 V, assuming that the lowest limit of the detection of Glu in the present study was the concentration of around 1.0×10^{-8} mol dm^{-3}. This supports the fact that membrane transport of Glu was hardly observed if concentration gradient was used as a driving force.

From the permselectivities expressed by the present membranes, they were not enough to be applicable in industries before long. Following ways are thought to be plausible ones to enhance membrane performance: (1) the PSf-Ac-Ala membrane should take a membrane form of nanofiber fabric, which would enhance both permselectivity and flux,[35] (2) chiral separation with the present membranes are operated by dual direction electrodialysis[22,26] or cascade multi-stage electrodialysis processes.[27]

Conclusions

Polysulfones bearing a derivative of alanyl residue as a chiral selector were prepared by reaction of benzylamine-modified polysulfones with N-α-acetyl-D-alanine or N-α-acetyl-L-alanine. The specific rotation ($[\alpha]_D$) of the polysulfone having the D-alanyl residue (PSf-Ac-D-Ala) was 2.87 deg cm^2 g^{-1} (c = 1.00 g/dL in DMF) and that with L-alanyl residue (PSf-Ac-L-Ala) was -2.36 deg cm^2 g^{-1}, which indicated that the chiral selector residues were successfully incorporated into the polysulfone. Both the modified polysulfone gave durable self-standing membranes. PSf-Ac-D-Ala membrane preferentially adsorbed the D-isomer of Glu from a racemic mixture of Glu and *vice versa*; that is, L-Glu was selectively incorporated into PSf-Ac-L-Ala. The chiral separation ability was investigated by applying a potential difference as a driving force for membrane transport. The membrane performance was greatly dependent on the applied potential difference and a wide range of permselectivity was attained by

adjusting the applied potential difference. At the applied potential difference of 18.0 V, the permselectivities for the membranes reflected their adsorption selectivity, in other words, the permselectivity of PSf-Ac-D-Ala toward D-Glu ($\alpha_{D/L}$) was determined to be 1.40, and that of PSf-Ac-L-Ala toward the L-isomer ($\alpha_{L/D}$) to be 1.48.

Keywords: alanyl residue; chiral selector; chiral separation; membrane; optical resolution; permselectivity; polysulfone

[1] D. Voet, J. G. Voet, *Biochemistry*, Wiley & Sons, New York, 1990.

[2] T. McKee, J. R. McKee, *Biochemistry The Molecular Basis of Life*. 3rd ed., WCB/McGraw-Hill, Boston, 2003.

[3] W. S. Knowles, *Angew. Chem. Int. Ed.*, **2002**, 41, 1998.

[4] R. Noyori, *Angew. Chem. Int. Ed.*, **2002**, 41, 2008-2022.

[5] K. B. Sharpless, *Angew. Chem. Int. Ed.*, **2002**, 41, 2024-2032.

[6] *Asymmetric Synthesis – The Essentials*. 2nd. ed.; M. Christmann, S. Bräse, Eds., Wiley-VCH, Weinheim, 2008.

[7] Asymmetric synthesis and application of α-amino acids (ACS Symposium Series 1009); V. A. Soloshonok, K. Izawa, Eds., ACS, Washington DC, 2009

[8] C. A. M. Afonso, J. G. Crespo, *Angew. Chem. Int. Ed.*, **2004**, 43, 5293.

[9] N. M. Maier, W. Lindner, *Anal. Bioanal. Chem.*, **2007**, 389, 377.

[10] R. Xie, L.-Y. Chu, J. G. Deng, *Chem. Soc. Rev.*, **2008**, 37, 1243.

[11] A. Higuchi, M. Tamai, Y.-A. Ko, Y. Tagawa, Y.-H. Wu, B. D. Freeman, J.-T. Bing, Y. Chang, Q.-D. Lin, *Polymer Reviews*, **2010**, 50, 113.

[12] M. Newcomb, J. L. Toner, R. C. Helgeson, D. J. Cram, *J. Am. Chem. Soc.*, **1979**, 101, 4941.

[13] T. Shinbo, T. Yamaguchi, H. Yanagishita, K. Sakaki, D. Kitamoto, M. Sugiura, *J. Membr. Sci.*, **1993**, 84, 241.

[14] J. T. F. Keurentjes, L. J. W. M. Nabuurs, E. A. Vegter, *J. Membr. Sci.*, **1996**, 113, 351.

[15] P. J. Pickering, J. B. Chaudhuri, *J. Membr. Sci.*, **1997**, 127, 115.

[16] A. Maximini, H. Chmiel, H. Holdik, N. W. Maier, *J. Membr. Sci.*, **2006**, 276, 221.

[17] A. Maruyama, N. Adachi, T. Takatsuki M. Torii, K. Sanui, N. Ogata, *Macromolecules*, **1990**, 23, 2748.

[18] T. Kakuchi, T. Takaoka, K. Yokota, *Polym. J.*, **1990**, 22, 199.

[19] T. Masawaki, M. Sasai, S. Tone, *J. Chem. Eng. Jpn.*, **1992**, 25, 33.

[20] T. Aoki, S. Tomizawa, E. Oikawa, *J. Membr. Sci.*, **1995**, 99, 117.

[21] S. Tone, T. Masawaki, K. Eguchi, *J. Membr. Sci.*, **1996**, 118, 31.

[22] M. Yoshikawa, J. Izumi, T. Ooi, T. Kitao, M. D. Guiver, G. P. Robertson, *Polym. Bull.*, **1998**, 40, 517.

[23] K. Taki, I. Arita. M. Satoh, J. Komiyama, *J. Polym. Sci.: Part B: Polym. Phys.*, **1999,** 37, 1035.

[24] A. Dzgoev, K. Haupt, *Chirality*, **1999**, 11, 465.

[25] J. Romero, A. L. Zydney, *J. Membr. Sci.*, **2002**, 209, 107.

[26] M. Yoshikawa, J. Izumi, *Macromol. Biosci.*, **2003**, 3, 487.

[27] A. Higuchi Y. Higuchi K. Furuta, B. O. Yoon, M. Hara, S. Maniwa, M. Saitoh, K. Sanui, *J. Membr. Sci.*, **2003**, 221, 207.

[28] E. Miyako, T. Maruyama, N. Kamiya M. Goto, *J. Am. Chem. Soc.*, **2004**, 126, 8622.

[29] M. Teraguchi, K. Mottate, S.-Y. Kim, T. Aoki, T. Kaneko, S. Hadano, T. Masuda, *Macromolecules*, **2005**, 38, 6367.

[30] M. Yoshikawa, K. Hanaoka, M. D. Guiver, G. P. Robertson, *Membrane*, **2005**, 30, 219.

[31] Y. Matsuoka, N. Kanda, Y. M. Lee, A. Higuchi, *J. Membr. Sci.*, **2006**, 280, 116.

[32] M. Yoshikawa, K. Murakoshi, T. Kogita, K. Hanaoka, M. D. Guiver, G. P. Robertson, *Eur. Polym. J.*, **2006**, 42, 2532.

[33] M. Nakagawa, Y. Ikeuchi, M. Yoshikawa, *Polymer*, **2008**, 49, 4612.

[34] Y. Ikeuchi, M. Nakagawa, M. Yoshikawa, *J. Polym. Sci.: Part A: Polym. Chem,.* **2009**, 47, 2530.

[35] Y. Sueyoshi, C. Fukushima, M. Yoshikawa, *J. Membr. Sci.*, **2010**, 357, 90.

[36] M. Yoshikawa, H. Hara, M. Tanigaki, M. Guiver, T. Matsuura, *Polym. J.*, **1992**, 24, 1049.

[37] M. Yoshikawa H. Hara, M. Tanigaki, M. Guiver, T. Matsuura, *Polymer*, **1992**, 33, 3805.

[38] M. Yoshikawa, K. Tsubouchi, M. D. Guiver, G. P. Robertson, *J. Appl. Polym. Sci.*,

1999, 74, 407.

[39] M. Yoshikawa A. Niimi, M. D. Guiver, G. P. Robertson, *Sen'I Gakkaishi*, **2000**, 56, 272.

[40] G. P. Robertson, M. D. Guiver, F. Bilodeau, M. Yoshikawa, *J. Polym. Sci.:Part A: Polym. Chem.*, **2003**, 41, 1316.

[41] K. Taniwaki, A. Hyakutake, T. Aoki, M. Yoshikawa, M. D. Guiver, G. P. Robertson, *Anal. Chim. Acta.*, **2003**, 489, 191.

[42] J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents*, 4th ed., Wiley, New York, 1986.

[43] L. A. Harwood, T. D. W. Claridge, *Introduction to organic spectroscopy*, Oxford University Press, Oxford, 1997.

Figure Captions

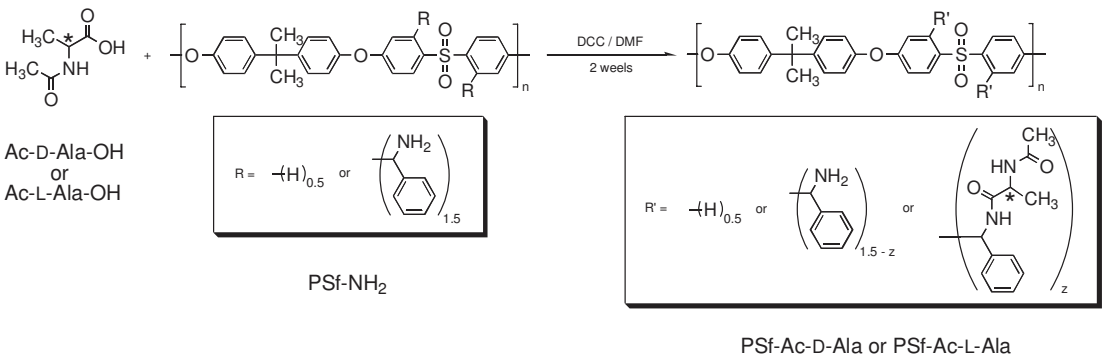
Figure 1. Synthetic scheme of modified polysulfone, PSf-Ac-Ala.

Figure 2. ^{1}H NMR spectrum of PSf-Ac-D-Ala (300 MHz, DMSO-d_6).

Figure 3. TGA curves of (a) PSf-Ac-D-Ala and (b) PSf-Ac-L-Ala.
(Heating rate, 10 °C min^{-1}.)

Figure 4. Time-transport curves of a racemic mixture of Glu through (a) PSf-Ac-D-Ala and (b) PSf-Ac-L-Ala membranes at ΔE = 18.0 V. (Operating temperature, 40 °C.)

Figure 5. Influence of applied potential difference on enantioselective electrodialysis of a racemic mixture of Glu through (a) PSf-Ac-D-Ala and (b) PSf-Ac-L-Ala membranes.



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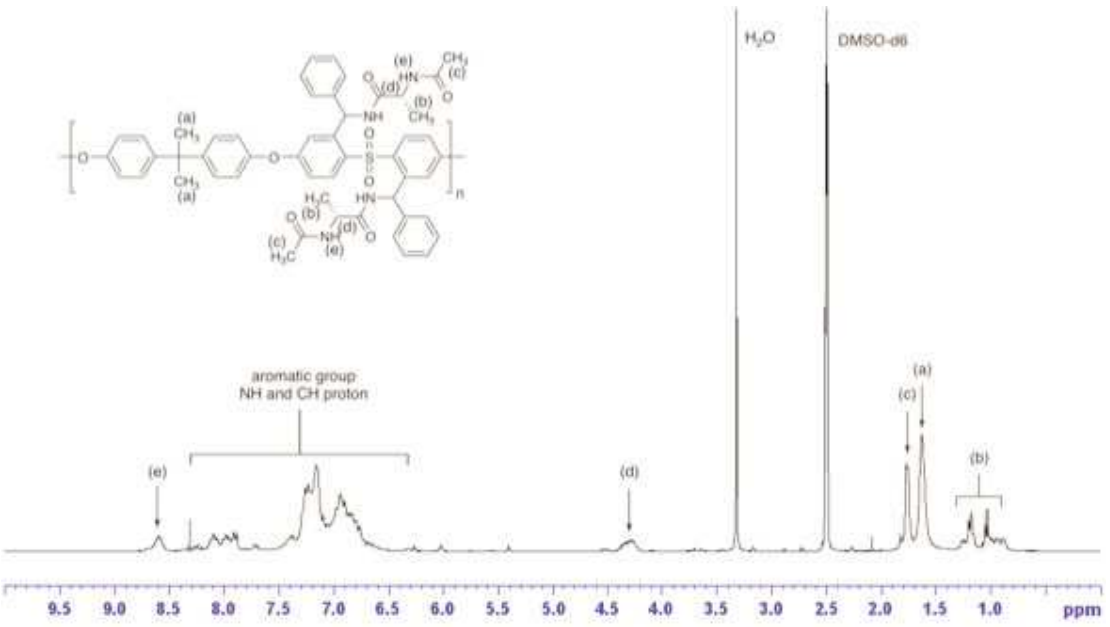

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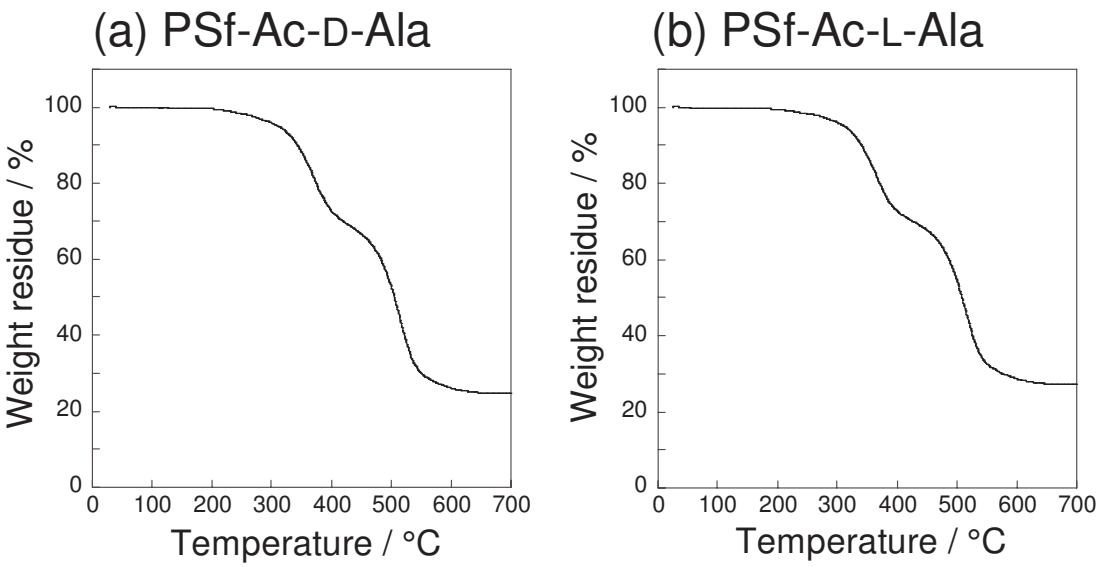

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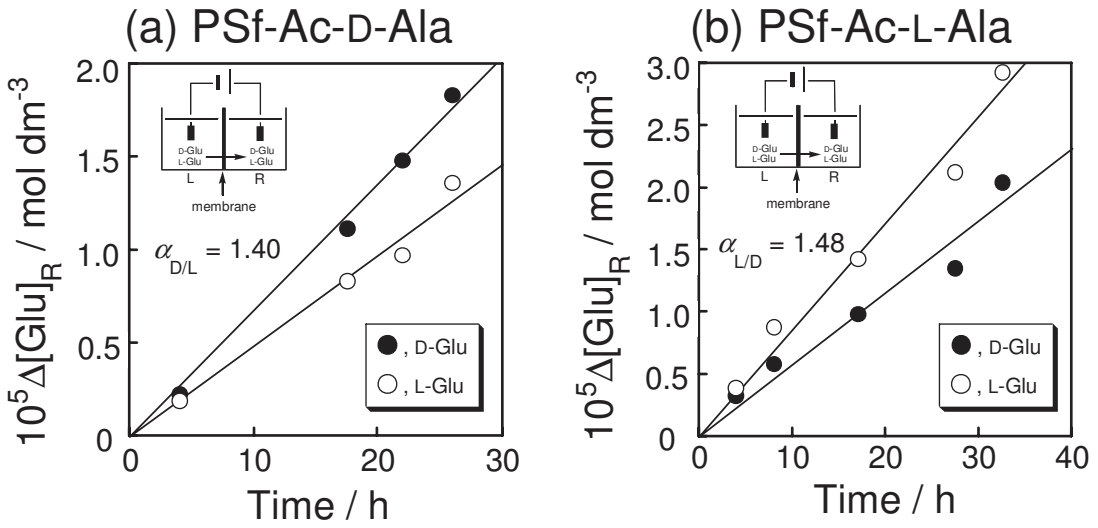

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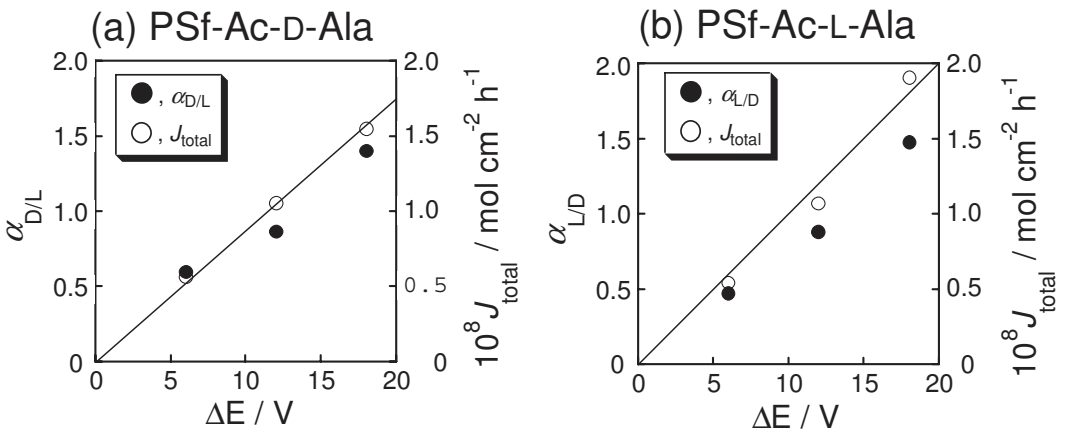

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Table 1. Syntheses of Modified Polysulfone (PSf-Ac-Ala)[a]

Exp. No.	$PSf\text{-}NH_2$ g (unit mol)	Ac-D-Ala-OH g (mol)	Ac-L-Ala-OH g (mol)	DCC g (mol)	Yield g (%)	z DS^b (%)
1[c]	1.000 (1.666×10^{-3})	0.374 (2.852×10^{-3})	– –	0.588 (2.850×10^{-3})	1.07 (83.5)	1.12 (74.7)
2[d]	1.000 (1.666×10^{-3})	– –	0.373 (2.845×10^{-3})	0.594 (2.879×10^{-3})	0.83 (64.8)	1.26 (84.0)

[a] in DMF; polymerization time, 2 weeks.

[b] Degree of substitution.

[c] Reaction temp., 25 °C.

[d] Reaction temp., ambient temp.

Table 2. Specific rotations of chiral selector and PSf-Ac-Ala*

	$[\alpha]_D$
	deg cm^2 g^{-1}
Ac-D-Ala-OH	27.81
Ac-L-Ala-OH	-27.18
PSf-Ac-D-Ala	2.87
PSf-Ac-L-Ala	-2.36

* in DMF; c = 1.00 g dL^{-1}; L = 10 cm.

Table 3. Adsorption selectivity of racemic mixture of Glu in PSf-Ac-Ala membranes in EtOH/H_2O

Membrane	D-Glu		L-Glu		$S_{A(D/L)}$	$S_{A(L/D)}$
	(D-Glu)/mem. mol/g-mem.	(D-Glu)/(CRU)*	(L-Glu)/mem. mol/g-mem.	(L-Glu)/(CRU)*		
PSf-Ac-D-Ala	6.83×10^{-5}	4.97×10^{-2}	3.84×10^{-5}	2.80×10^{-2}	1.90	0.53
PSf-Ac-L-Ala	3.53×10^{-5}	2.62×10^{-2}	6.78×10^{-5}	5.04×10^{-2}	0.50	2.00

* Constitutional repeating unit of PSf-Ac-Ala membrane.

Table of Contents

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