Optical Resolution of Racemic Amino Acid Derivatives with Chiral Polyamides Bearing Glutamyl Residue as a Diacid Component

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ABSTRACT: Novel chiral polyamides with chiral environment in their main chains were obtained from aromatic diamine, 4,4′-diaminodiphenylmethane (DADPM), and the D-isomer or the L-isomer of N-α-protected glutamic acid, such as N-α-benzyloxycarbonyl-D-glutamic acid (Z-D-Glu-OH) or N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu-OH), in the presence of triphenyl phosphite (TPP). Two types of newly prepared polyamide showed optical rotation, implying that there were asymmetric carbons in their main chains. Circular dichroism studies demonstrated that resulting chiral polyamides took a helical structure. Optical resolution ability of those two types of polyamide was studied by adopting potential difference as a driving force for membrane transport. Membranes showed permselectivity toward racemic mixture of N-α-acetyltryptophan (Ac-Trp). The permselectivity was dependent on the absolute configuration of diacid component. The permselectivity was expressed by diffusivity selectivity, which was determined by the presence of chiral helicity. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 857–865, 2012

Key words: chiral separation; chiral polyamide; membrane; optical resolution; permselectivity; polyamide

INTRODUCTION

Chirality plays an important role in biological processes.[1] Based on this, the production of enantiomerically pure compounds is an important process in various industries, dealing with pharmaceuticals, agrochemicals, fragrances, food additives, and so forth. There are a couple of ways to obtain optically pure compounds; one is asymmetric synthesis and the other is the optical resolution of racemic mixtures. Asymmetric synthesis of enantiomerically pure compounds is thought to be an ultimate way to obtain those compounds and has been intensively studied[2–4]; its development is, however, still slow. The resolution of racemates is still promising and mighty method to get optically pure enantiomers. There are various optical resolution methods, such as crystallization resolution, kinetic resolution, chromatographic separation, and membrane-based separation. Among those chiral separation methods, liquid chromatography (LC), which is categorized as chromatographic separation, is regarded as an efficient separation method for an industrial-scale resolution of racemates, though it is a batch process. Adopting simulated moving bed chromatography, optical resolution can be continuously carried out. Chiral separation of racemic mixtures with membranes is regarded as an alternative promising method to obtain optically pure enantiomers.[5–8] Membrane-based chiral separation can be performed continuously under mild conditions and can be ecologically and economically competitive to other optical resolution methods.

Membrane-based chiral separation is divided into a couple of membrane systems, such as liquid[9–13] and polymeric (solid)[14–40] membranes. In a liquid membrane system, a carrier with chiral environment plays an important role like a transporter in biological processes. In a polymeric membrane system, optical resolution was mostly carried out by adopting a membrane with a chiral environment or that functionalized by a chiral selector. Polymeric filtration membrane with no chiral environment also contributed to optical resolution in cooperation with enantioselective binding agents, such as bovine serum albumin.[24] Enantioselective polymeric membrane with enzyme[25] or nonenantioselective one with enzyme[29,30] showed optical resolution ability, which was categorized as kinetic resolution. From results of optical resolution with synthetic membranes reported so far,[9–40] there can be found chiral

recognition sites or chiral environment in those optical resolution systems, even though the membrane system or methodology for optical resolution was different.

The authors' research group focused their attentions on optical resolution of racemic mixtures with membranes, optical resolution has been studied using molecularly imprinted membranes,[18,26] molecularly imprinted nanofiber ones to obtain high throughput,[33,40] optical resolution membranes from natural polymer[34] or derivative of natural polymer,[39] and synthetic polymeric membranes consisting of amino acid residue as a diacid component.[36,38] Chiral polyamide membranes consisting of L-glutamyl residue as a diacid component preferentially transported the derivative of D-amino acid, which was selectively adsorbed in the membranes, at the optimum potential difference.[36,38] From the results observed in optical resolution with chiral polyamides, it can be expected that chiral polyamide membranes consisting of D-amino acid residue as a diacid component showed opposite permselectivity, which was expressed by that consisting of L-amino acid residue. To this end, novel chiral polyamides consisting of an amino acid residue were prepared from N-α-benzyloxycarbonyl-D-glutamic acid (Z-D-Glu-OH) or N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu-OH) as a diacid component and 4,4′-diaminodiphenylmethane (DADPM) as a diamine component in the presence of triphenyl phosphite (TPP),[41–46] and their optical resolution ability was studied.

EXPERIMANTAL

Materials

N-α-Benzyloxycarbonyl-D-glutamic acid (Z-D-Glu-OH), N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu-OH), TPP, 1,1,1,3,3,3,-hexafluoro-2-propanol (HFIP), anhydrous LiCl, N-α-acetyl-D-tryptophan (Ac-D-Trp), N-α-acetyl-L-tryptophan (Ac-L-Trp), methanol, 1-octanethiol, and ethanol were obtained from commercial sources and used as received. DADPM was purified by crystallization from H_2O.[47] 1-Methyl-2-pyrrolidinone (NMP), pyridine, and N,N-dimethylformamide (DMF) were purified by the usual methods.[48] Water purified with an ultrapure water system (Simpli Lab, Millipore S.A., Molsheim, France) was used.

General polycondensation procedure

Requisite amounts of chemicals were placed in a reaction flask fitted with a condenser and thermometer.[41–46] The mixture was magnetically stirred at 80°C for 3 h. The resulting viscous solution was poured into methanol under rapid stirring, and the

precipitate product was washed with methanol and dried in vacuo.

Characterization of chiral polyamides

The inherent viscosity was determined with an Ubbelohde viscometer at a concentration of 5.0×10^{-3} g cm^{-3} in DMF at 25°C. The IR spectra were recorded by using a Perkin–Elmer Spectrum GX; 64 scans at a resolution of 4 cm^{-1} were collected with membrane, which was prepared from HFIP solution. The ^{1}H-NMR (500 MHz) were recorded in HFIP-d_2 using Bruker DRX-500 with tetramethylsilane as an internal standard. The specific rotations were obtained with Horiba SEPA-200 polarimeter at 589 nm at ambient temperature in DMF. Circular dichroism (CD) and UV–visible spectra were recorded on JASCO J-720 Spectropolarimeter with membranes, which were prepared from HFIP solution cast on a quartz plate. Differential scanning calorimetry (DSC) measurement was performed with Shimadzu DSC-60. The heating rate was fixed to be 20°C min^{-1}, and the sample was purged with nitrogen at a flow rate of 50 cm^3 min^{-1}. The thermal stability of the polymer was evaluated on a Hi-Res Modulated TGA 2950 (TA instruments) under nitrogen at a heating rate of 10°C min^{-1}. Tensile stress–strain measurement was performed with TENSILON/UTM-II-5H (Orientec) with a rectangular-shaped film (5 mm wide), clamped between a pair of chucks, which were 15 mm apart in the unstretched state. The sample thickness was around 12 μm. Obtained results were averaged over 10 membrane samples. The chiral recognition of the prepared polyamides was evaluated by surface plasmon resonance (SPR) using an SPR instrument (SPR670S, Nippon Laser Electronics Laboratory).[49]

Membrane preparation

A 0.100 g of chiral polyamide was dissolved in 1.0 cm^3 of DMF. The polymer solution thus prepared was cast onto a glass plate with an applicator (casting thickness, 0.254 mm), and the solvent was allowed to evaporate at 50°C for 1 day. The thickness of the membrane was ∼ 12 μm.

Enantioselective electrodialysis

A membrane (area, 3.0 cm^2) was fixed tightly with Parafilm between two chambers of a permeation cell. A 50 vol % of aqueous ethanol solution of racemic Ac-Trp's was placed in each chamber of a permeation cell, of which solution volume was 40 cm^3 each. Each concentration of racemic Ac-Trp was fixed at 1.0×10^{-3} mol dm^{-3}. The electrodialysis was carried out with an applied potential difference
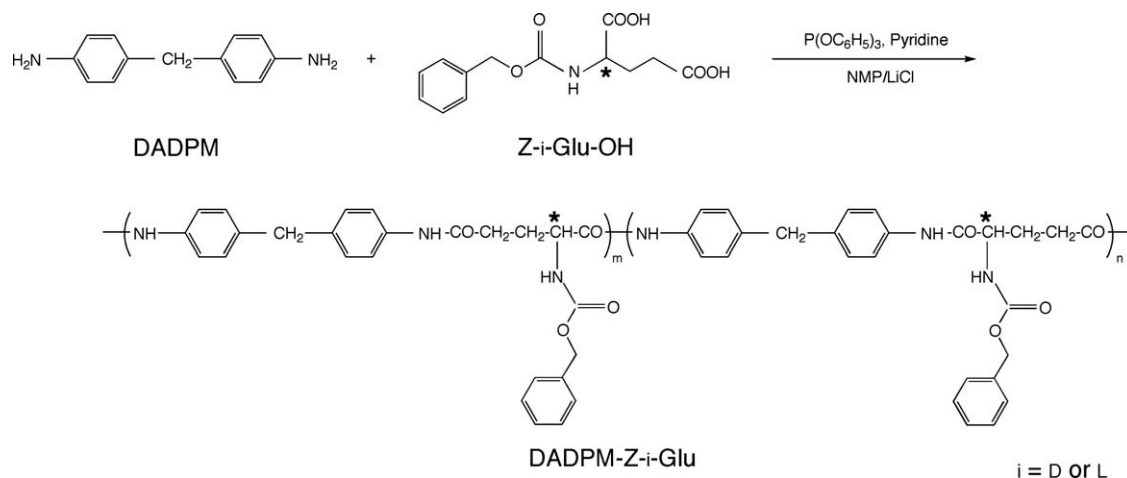
Figure 1 Synthetic scheme of chiral polyamides from DADPM and Z-i-Glu-OH.

of 9.0 V between platinum electrode (1.0 cm^2; distance between platinum electrodes, 65 mm) at 40°C with stirring. An aliquot was drawn from the permeate side at each sampling time. The amounts of Ac-D-Trp and Ac-L-Trp that transported through the membrane were determined by LC [JASCO PU 1580, equipped with a UV detector (JASCO UV 1570)] using CHIRALPAK MA(+) column [50 × 4.6 mm (i.d.)] (Daicel Chemical Ind.). A mixture of acetonitrile and aqueous copper sulfate solution was used as a mobile phase.

The flux, J_D and J_L (mol cm^{-2} h^{-1}) is defined as:

$$J = Q/At \tag{1}$$

where Q (mol) is the amount of transported Ac-Trp, A (cm^2) is the effective membrane area, and t (h) is the time. Hereafter, subscripts D and L mean the D-isomer of Ac-Trp and the L-isomer of Ac-Trp, respectively.

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

$$\alpha_{i/j} = (J_i/J_j)/([i - \text{Glu}]/[j - \text{Glu}]) \tag{2}$$

RESULTS AND DISCUSSION

Polycondensation

In our previous study,[36,38] chiral polyamides were prepared by means of TPP, so that carboxylic acid would be activated to react with aromatic amino group. In the present study, similar recipe[36,38] was adopted to obtain two types of chiral polyamide
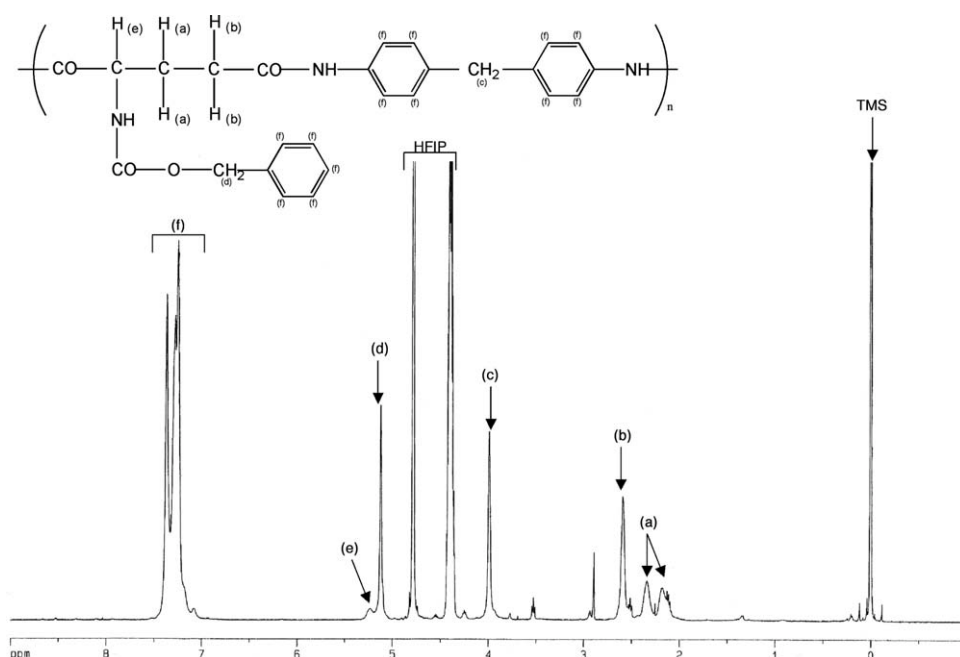

Figure 2 ^{1}H-NMR spectrum of chiral polymaide from DADPM and Z-D-Glu (500 MHz and HFIP-d_2).

TABLE I
Polycondensation Reaction of DADPM and Z-Glu-OH by Means of Triphenyl Phosphite[a]

Exp. no.	Monomer conc.[b] (mol dm^{-3})	DADPM [g (mol)]	Z-D-Glu-OH [g (mol)]	Z-L-Glu-OH [g (mol)]	Triphenyl phosphite [g (mol)]	NMP/Py (cm^3/cm^3)	LiCl (g)	Yield [g (%)]	η_{inh}[c] (g^{-1} cm^3)
1	3.00×10^{-1}	0.8922 (4.500×10^{-3})	1.2658 (4.500×10^{-3})	–	2.7925 (9.000×10^{-3})	12.0/3.0	0.600	1.982 (91.8)	58
2	5.00×10^{-1}	0.9913 (5.000×10^{-3})	1.4065 (5.000×10^{-3})	–	3.1028 (1.000×10^{-2})	8.0/2.0	0.400	2.249 (93.8)	75
3	6.00×10^{-1}	0.9517 (4.800×10^{-3})	1.3502 (4.800×10^{-3})	–	2.9787 (9.600×10^{-3})	6.4/1.6	0.320	2.052 (89.1)	90
4	6.00×10^{-1}	0.3569 (1.800×10^{-3})	0.5063 (1.800×10^{-3})	–	1.1170 (3.600×10^{-3})	2.4/0.6[d]	0	0.739 (85.6)	21
5	6.00×10^{-1}	0.9517 (4.800×10^{-3})	–	1.3502 (4.800×10^{-3})	2.9787 (9.600×10^{-3})	6.4/1.6	0.320	2.050 (89.1)	99

[a] Polymerization temp., 80°C; polymerization time, 3 h.
[b] Monomer conc. = $[DADPM]_0 = [Z\text{-}i\text{-}Glu\text{-}OH]_0$ (i = D or L).
[c] Measured at a concentration of 5.0×10^{-3} g cm^{-3} in DMF at 25°C.
[d] DMF/Py.

from DADPM as a diamine monomer and Z-D-Glu-OH or Z-L-Glu-OH as a diacid one.

The polycondensation scheme is shown in Figure 1. In IR spectra, the amide I bands were observed at 1670 cm^{-1} in polyamide from DADPM and Z-D-Glu-OH and at 1669 cm^{-1} in that from DADPM and Z-L-Glu-OH. Figure 2 shows a ^{1}H-NMR spectrum of DADPM-Z-D-Glu. Small amount of remained reaction solvent, NMP, was observed (the signals at 2.1, 2.5, 2.9, and 3.5 ppm). Similar ^{1}H-NMR spectrum was observed in that of DADPM-Z-L-Glu. From those ^{1}H-NMR spectra, it can be confirmed that the amino protecting group, benzyloxycarbonyl moiety, was preserved in the obtained polyamides. As shown in Figure 1, there would be a couple of ways for diacid monomer, Z-Glu-OH, to react with amino terminal of polyamide during the polycondensation reaction. However, in the present study, stereoregularity of those two types of chiral polyamide was hardly determined. The IR and ^{1}H-NMR spectra led to the conclusion that the expected polyamides were obtained from DADPM and Z-Glu-OH.

Previous study led to the conclusion that NMP/LiCl was determined to be a suitable medium for the polycondensation.[36] In the present study, NMP/LiCl was also adopted as a solvent system for the polycondensation reaction of aromatic diamine monomer and Z-Glu-OH. The suitable monomer concentration for the polyamide preparation was studied adopting Z-D-Glu-OH as an acid monomer. The viscosity of polymer solution was used as an index. Table I summarizes the results of polycondensation reaction of DADPM and Z-Glu-OH. After the polycondensation reaction at the monomer concentration of 6.00×10^{-1} mol dm^{-3} (Exp. No. 3 in Table I), the viscosity of the reaction mixture was too high to be stirred well. From this, it was judged that not only soluble polyamide but also insoluble polyamide gel would be obtained at the monomer concentration of over 6.00×10^{-1} mol dm^{-3}. In the present polycondensation reaction, the suitable monomer concentration was determined to be 6.00×10^{-1} mol dm^{-3}. The obtained chiral polyamides were dissolved not only in polycondensation solvent system, NMP/LiCl, but also in DMF and HFIP. From the fact mentioned earlier, polycondensation reaction was carried out in DMF under the determined suitable monomer concentration of 6.00×10^{-1} mol dm^{-3} (Exp. No. 4 in Table I). The viscosity of polymer solution for Exp. No. 4 was lower than that of Exp. No. 3 in Table I. This might be explained by the plausible speculation that solubility of the obtained polyamide in NMP/LiCl was higher than that in DMF.

The chiral polyamide consisting of L-glutamyl moiety, such as DADPM-Z-L-Glu, was prepared under the same polycondensation conditions for
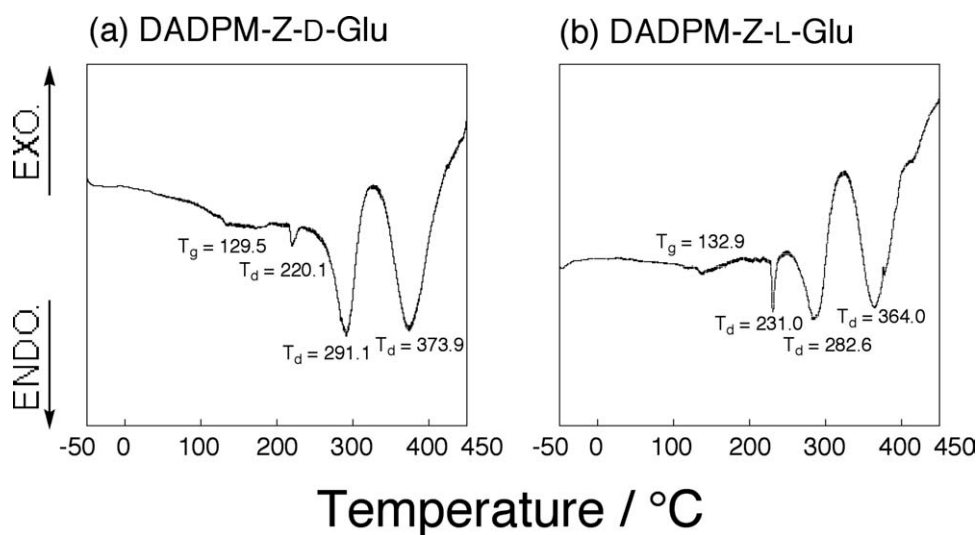
Figure 3 DSC curves of (a) DADPM-Z-D-Glu and (b) DADPM-Z-L-Glu (heating rate, 20°C min^{-1}; N$_2$ flow, 50 cm^3 min^{-1}).

antipode chiral polyamide (Exp. No. 5 in Table I). DADPM-Z-L-Glu, which was prepared under the suitable monomer concentration of 6.0×10^{-1} mol dm^{-3}, gave similar polymer solution viscosity of that for Exp. No. 3 in Table I.

Thermal properties

Figure 3 shows DSC thermographs of two types of newly prepared polyamide. The glass transition temperature (T_g) for DADPM-Z-D-Glu was determined to be 129.5°C and that for DADPM-Z-L-Glu to be 132.9°C. The chiral polyamide from DADPM and N-α-benzoyl-L-glutamic acid (benzoyl-L-Glu-OH) gave the T_g of around 91.4°C.[38] From this, it can be revealed that the protecting group of benzyloxycarbonyl moiety (Z) would give higher T_g than that of

benzoyl one. The flexibility of polyamide consisting of Z-Glu, of which protecting group of Z-moiety is though to be more bulky than benzoyl one, might be depressed more than that of DADPM-Benzoyl-L-GLu[50,51]; as a result, the present polyamides gave higher T_g values than that of previous DADPM-Benzoyl-L-Glu.

Figure 4 shows thermogravimetric analysis thermographs for those polyamides obtained in the present study. From those thermographs, it was concluded that thermal stability of those polyamides was not so good, which is due to the fact that the amino group in the glutamyl residue is protected by benzyloxycarbonyl (Z) moiety. However, comparing with the thermal stability of the previous DADPM-Benzoyl-L-Glu, the present polyamides were more stable, and the decomposition temperature of those
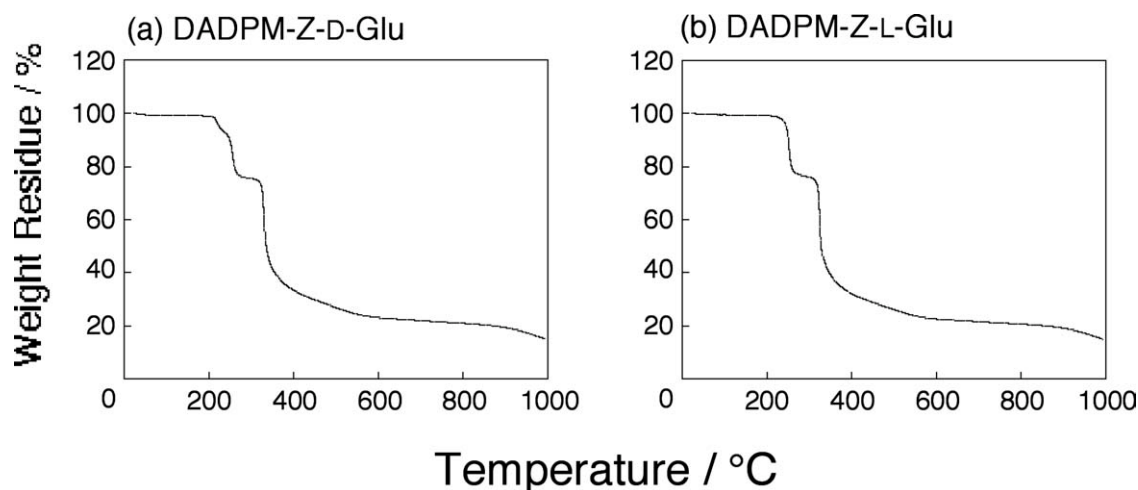

Figure 4 Thermogravimetric analysis thermographs of (a) DADPM-Z-D-Glu and (b) DADPM-Z-L-Glu (heating rate, 10°C min^{-1}).
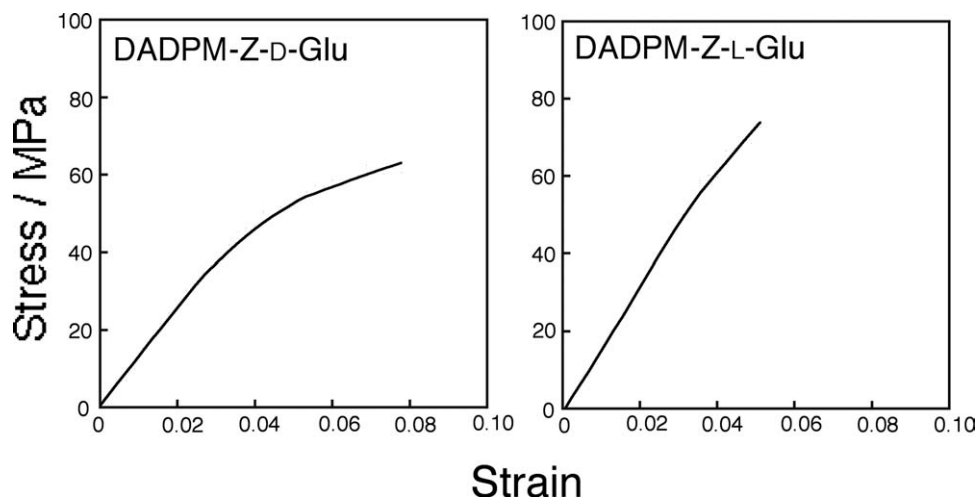
Figure 5 Stress–strain curves of chiral polyamides.

was around 50°C higher than that of DADPM-ben-zoyl-L-Glu. This was also due to the depression of the flexibility of DADPM-Z-Glu as mentioned earlier.

Mechanical properties

The newly obtained chiral polyamides gave durable self-standing membranes. Mechanical properties of the two types of polyamide were studied. The stress–strain curves of the membranes are given in Figure 5. Mechanical properties of the present poly-amides are summarized in Table II together with common polymers.[52] The mechanical properties of the present polyamides were similar to that of chiral polyamide from DADPM and benzoyl-L-Glu-OH.[38] In the present study, optical resolution ability was investigated adopting the forms of self-standing membranes.

Chiroptical properties

The optical rotations ($[\alpha]_D$) of the two types of chiral polyamide newly prepared in the present study are given in Table III, together with those of correspond-

ing diacid monomer, Z-D-Glu-OH and Z-L-Glu-OH. Results summarized in Table III revealed that opti-cally active polyamides were successfully obtained via polycondensation reaction activated by TPP at 80°C. The optical rotations for these polyamides were opposite to those of the corresponding mono-mers. In addition, the polyamide consisting of Z-D-glutamyl residue gave opposite in sign to that having Z-L-glutamyl residue.

Figure 6 shows CD and UV–vis spectra of those two types of chiral polyamide membrane. The opti-cal rotations summarized in Table III and CD signals are attributed to the helicity of the polyamide main chains with predominantly one-handed screw sense. The membranes having main chains with different absolute configuration, such as the membrane from polyamide having Z-D-Glu residue and that with Z-L-Glu one, exhibited oppositely signed optical rotations and mirror-image CD signals each other. This result indicates that those polyamide mem-branes take helical structures with opposite screw sense mutually and that the helix sense of the mem-brane was controlled by the absolute configuration of the chiral group in the main chain.

It can be expected that the membranes from the present polyamides showed optical resolution

TABLE II
Ultimate Mechanical Properties of Chiral Polyamides

Membrane (film)	Tensile strength at break (MPa)	Elongation at break (%)	Tensile modulus (GPa)
DADPM-Z-D-Glu	57	6.9	1.1
DADPM-Z-L-Glu	72	5.4	1.5
Polystyrene[a]	50	2.5	3.4
Poly(methyl methacrylate)[a]	65	10.0	3.2
Nylon 66[a]	80	200.0	2.0
Nylon 6[a]	75	300.0	1.9

[a] Cited from Ref. 52.

TABLE III
Specific Rotations of Chiral Polyamides and Their Corresponding Diacid Monomers

	$[\alpha]_D$
Z-D-Glu-OH[a]	21.6
DADPM-Z-D-Glu[b]	−12.3
Z-L-Glu-OH[a]	−21.3
DADPM-Z-L-Glu[b]	14.4

[a] In DMF, $c = 5.00$ g dL^{-1}, $L = 10$ cm.
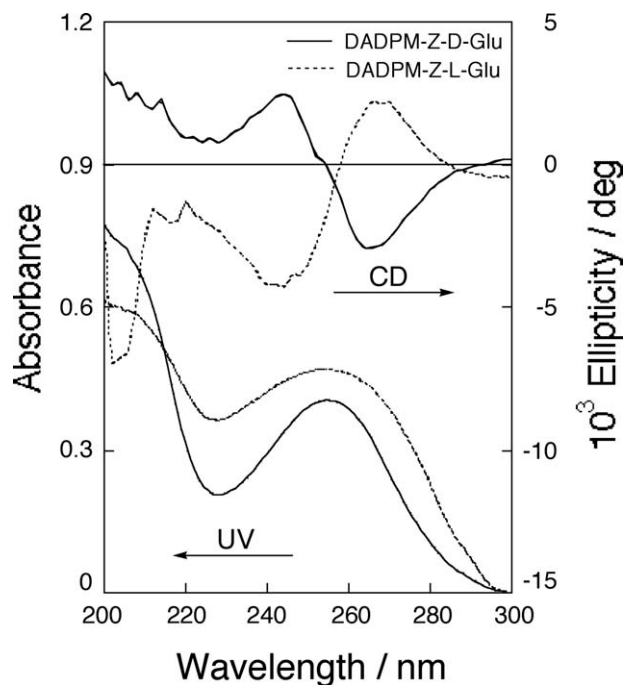[b] In DMF, $c = 1.00$ g dL^{-1}, $L = 10$ cm.

Figure 6 CD and UV–vis spectra of chiral polyamide membrane.

ability. Because preferential interaction or mobility toward an enantiomer against the corresponding antipode would be expected from the fact that chiral environment was introduced into the main chain.

Chiral recognition ability estimated by SPR spectroscopy

The results obtained in the above chapter "Chiroptical properties" and the previous results[36,38] suggested that those two types of membrane newly obtained in the present study showed chiral recognition ability; DADPM-Z-D-Glu membrane was expected to show adsorption selectivity toward the L-isomer of amino acid and *vice versa*. In the present study, the chiral recognition ability was evaluated by SPR spectroscopy, which provides a rapid and facile evaluation method comparing with usual adsorption experiments, by adopting Ac-D-Trp and Ac-L-Trp as targeted enantiomers. Against expectation, those membranes hardly showed adsorption selectivity. Replacement of the protecting group of benzoyl moiety by that of benzyloxycarbonyl (Z) moiety might be the cause of depression of adsorption selectivity.

Enatioselective electrodialysis

As mentioned in the previous section, the two types of chiral membrane hardly showed adsorption selectivity, even though there was chiral environment in those membranes. However, optical resolution ability would be observed if the permselectivity was expressed by diffusivity selectivity, which was due to one-handed screw sense of those membranes like *in situ* depinanylsilylated phenylacetylene membranes without the presence of chiral moiety.[31] To this end, optical resolution ability of the present membranes was preliminarily studied. In the present study, the potential difference was applied as a driving force for optical resolution, membrane transport.

Figure 7 shows time-transport curves of racemic mixture of Ac-Trp through the present membranes at an applied potential difference of 9.0 V. The DADPM-Z-D-Glu membranes preferentially transported the
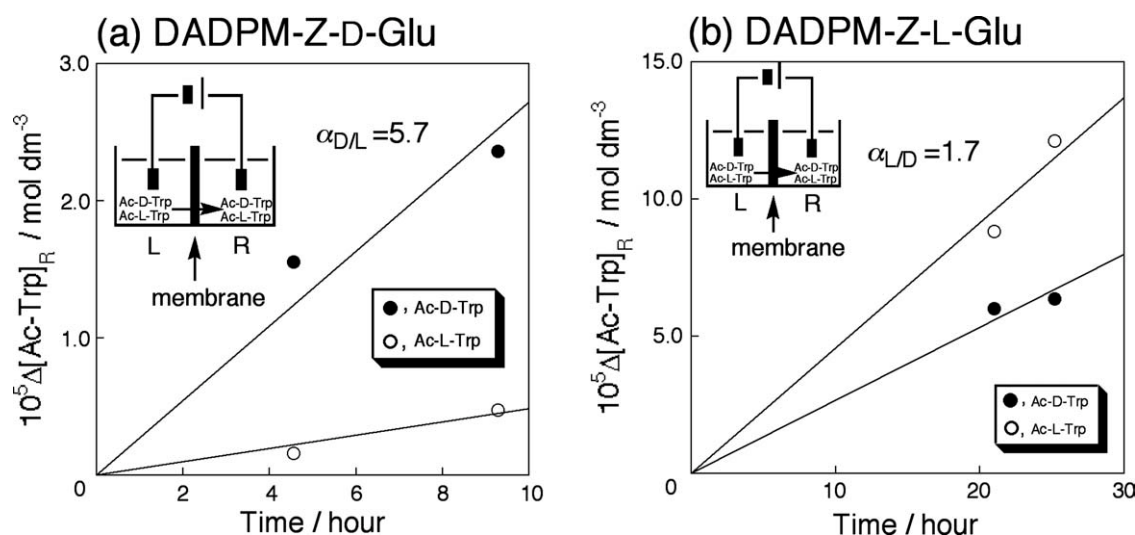

Figure 7 Time-transport curves of racemic mixture of Ac-Trp's through the membranes from (a) DADPM-Z-D-Glu and (b) DADPM-Z-L-Glu in aqueous ethanol at 40°C ($\Delta E = 9.0$ V).

D-isomer of Ac-Trp and its permselectivity, $\alpha_{D/L}$, was determined to be 5.7. Contrary to this, Ac-L-Trp was transported in preference to the corresponding D-isomer through the DADPM-Z-L-Glu membrane. The permselectivity toward Ac-L-Trp was determined to be 1.7. The results obtained in the present study revealed that the optical resolution ability was expressed by diffusivity selectivity due to one-handed screw sense of the membrane like depinanylsilylated phenylacetylene membranes.[31] In the preliminary study, two types of membrane did not give similar permselectivity; this might be due to membrane morphology determined by membrane preparation condition, difference in stereoregularity of polyamide, and so forth.

CONCLUSIONS

Novel chiral polyamides with chiral environment in their main chains were obtained from aromatic diamine, DADPM, and the D-isomer or the L-isomer of N-α-protected glutamic acid, such as N-α-benzyloxycarbonyl-D-glutamic acid (Z-D-Glu-OH) or N-α-benzyloxycarbonyl-L-glutamic acid (Z-L-Glu-OH), in the presence of TPP. Two types of newly prepared polyamide showed optical rotation, implying that there were asymmetric carbons in their main chains. CD studies demonstrated that resulting chiral polyamides took a helical structure. SPR spectroscopy study revealed that the present membranes hardly showed adsorption selectivity toward racemic mixture of N-α-acetyl-tryptophan (Ac-Trp). Optical resolution ability of those two types of polyamide was studied by adopting potential difference of 9.0 V as a driving force for membrane transport. Membranes showed permselectivity toward racemic mixture of N-α-acetyltryptophan (Ac-Trp). DADPM-Z-D-Glu membrane transported Ac-D-Trp in preference to the corresponding L-isomer and *vice versa*. The permselectivity toward Ac-D-Trp for DADPM-Z-D-Glu membrane was determined to be 5.7 and that toward the L-isomer for DADPM-Z-L-Glu to be 1.7. The permselectivity was expressed by diffusivity selectivity, which was determined by the presence of chiral helicity.

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