Open Journal of Polymer Chemistry, 2012, 2, 125-131
http://dx.doi.org/10.4236/ojpchem.2012.24017 Published Online November 2012 (http://www.SciRP.org/journal/ojpchem)

Chiral Polyamides Having L-Glutamyl Residue as a Component

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Received August 2, 2012; revised September 6, 2012; accepted September 16, 2012

ABSTRACT

Polyamides with chiral environment were obtained from aromatic diamine, 1,3-phenylenediamine (1,3-PDA) or 1,4-phenylenediamine (1,4-PDA), and N-α-benzoyl-L-glutamic acid (Benzoyl-L-Glu). The optical rotation ($[\alpha]_D$) for 1,3-PDA-Benzoyl-L-Glu was determined to be 3.7 deg cm^2 g^{-1}, while that for 1,4-PDA-Benzoyl-L-Glu to be 9.7 deg cm^2 g^{-1}. 1,3-PDA-Benzoyl-L-Glu showed adsorption selectivity toward D-Glu and its adsorption selectivity was determined to be 1.68. Contrary to this, 1,4-PDA-Benzoyl-L-Glu showed adsorption selectivity toward L-Glu and the adsorption selectivity toward L-Glu was determined to be 1.33. From those results, those two types of chiral polyamide are expected to applicable to chiral separation or chiral recognition.

Keywords: Adsorption Selectivity; Chiral Polyamide; Glutamyl Residue; Polyamide; Surface Plasmon Resonance (SPR) Spectroscopy

1. Introduction

Chirality plays an important role in biological processes [1,2]. A given enantiomer and the corresponding antipode often exhibit different pharmacological effects. It is often observed that a drug enantiomer gives the desired effect whereas the antipode does not give the desired pharmacological effect or exhibit toxicity. From this, the production of enantiomerically pure compounds is an important processes in various industries, involving pharmaceuticals, agrochemicals, fragrances, food additives, and so forth.

Among various separation methods, chiral separation with membranes is promising way since membrane separation can be carried out continuously under mild conditions. In addition to this, membrane separation is economically and ecologically competitive to other separation methods since membrane separation, excepting pervaporation, can be operated without phase transition. From articles on chiral separation by using membrane [3-6], there can be found chiral recognition sites or chiral environments in membranes or membrane separation processes.

The authors' research group studied molecularly imprinted polymers [7-11], polymeric materials bearing amino acid residues [12-16], and natural polymers [17-19] as membrane materials for chiral separation. In the present study, chiral polyamides were synthesized adopting N-α-benzoyl-L-glutamic acid (Benzoyl-L-Glu-OH) as a chiral building block and 1,3-phenylenediamine (1,3-PDA) or 1,4-phenylenediamine (1,4-PDA) as diamine component, which is expected to give a more rigid chiral polyamide than 4,4'-diaminodiphenylmethane (DADPM) [13].

2. Experimental

2.1. Materials

N-α-Benzoyl-L-glutamic acid (Benzoyl-L-Glu-OH), triphenyl phosphite (TPP), anhydrous LiCl, D-glutamic acid (D-Glu), L-glutamic acid (L-Glu), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and sodium azide (fungicide) were obtained from commercial sources and used as received. 1,3-Phenylenediamine (1,3-PDA) was purified by crystallization from diethyl ether [20] and 1,4-phenylenediamine (1,4-PDA) by sublimation under reduced pressure [21]. 1-Methyl-2-pyrrolidinone (NMP), pyridine (Py), and N,N-dimethylformamide (DMF) were purified by usual methods [22]. Water purified with an ultrapure water system (Simpli Lab, Millipore S. A., Molsheim, France) was used.

2.2. General Polycondensation

Requisite amounts of chemicals were placed in a reaction

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flask fitted with a condenser and thermometer. The mixture was magnetically stirred at 80˚C for 3 h. The resulting viscous solution was poured into methanol under rapid stirring, and the prescribed product was washed with methanol and dried *in vacuo* for 3 d.

2.3. Chracterizartion of the Chiral Polyamides

The inherent viscosity was determined with an Ubbelohde viscometer at a concentration of 5.0×10^{-3} g cm^{-3} in HFIP 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 a membrane prepared from HFIP solution. The ^{1}H NMR (500 MHz) spectrum was recorded in 1,1,1,3,3,3-HFIP-d$_2$ using a Bruker DRX-500 with tetramethylsilane (TMS) as an internal standard. 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}. Differential scanning calorimetry (DSC) 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}. 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 20 μm. Obtained results were averaged over 10 film samples. The specific rotations were obtained with Horiba SEPA-200 polarimeter at 589 nm at ambient temperature in DMF.

2.4. Adsorption Selectivity

The adsorption selectivity of the prepared polyamides was studied as follows; a gold-deposited glass plate was immersed in a 1.0×10^{-5} mol dm^{-3} solution of 1-octanthiol in ethanol for 30 min at ambient temperature prior to the film preparation. The film was prepared by spin-casting a 1.0 g dm^{-3} HFIP solution of the polyamide onto the pre-treated gold-deposited glass plate. The rotation speed for spin casting was 3000 rpm.

The adsorption selectivity of the prepared film toward racemic Glu was evaluated by surface plasmon resonance (SPR) spectroscopy. The change in incident angle ($\Delta\theta$) responding to the addition of substrate was recorded on the SPR apparatus (SPR670S, Nippon Laser and Electronics Laboratory). During the measurement, 0.02 wt% NaN$_3$ aqueous buffer was passed over the film surface at 5 mm^3 min^{-1}. The flow was periodically replaced with solutions of same buffer containing D-glutamic acid (D-Glu) or L-glutamic acid (L-Glu). The experiment was carried out at 27˚C.

3. Results and Discussion

3.1. Polycondensation

In the previous studies [12-14], chiral polyamides were prepared by means of TPP so that carboxylic acid could be activated to react with amino groups. In the present study, similar polycomdensation reaction method was adopted to obtain chiral polyamides from N-α-benzoyl-L-glutamic acid (Benzoyl-L-Glu-OH) and 1,3-phenylenediamine (1,3-PDA) or 1,4-phenylenediamine (1,4-PDA). In the previous study [13], the chiral polyamide was prepared from Benzoyl-L-Glu-OH and 4,4’-diaminodiphenylmethane (DADPM). As described in the introduction, chiral polyamides obtained in the present study were expected to show more rigid and more thermally stable ones than the previous one, DADPM-Benzoyl-L-Glu, which was obtained from DADPM and Benzoyl-L-Glu-OH [13].

The polycondensation scheme is shown in **Figure 1**. In the IR spectra, those two types of polyamide gave the amide I band at 1645 cm^{-1}.

^{1}H NMR spectrum for 1,3-PDA-Benzoyl-L-Glu is shown in **Figure 2** and that for 1,4-PDA-Benzoyl-L-Glu in **Figure 3**. From **Figures 2** and **3**, it can be confirmed that the amino protecting group of benzoyl moiety was preserved in those polyamides. The IR and ^{1}H NMR spectra led to the conclusion that the expected polyamides were obtained from Benzoyl-L-Glu-OH and 1,3-PDA or 1,4-PDA. However, stereo regularity of those two types of chiral polyamide was hardly determined.

The optimum reaction conditions for polycondensation for those polyamides were determined by using viscosity of polymer solution as an index. The results of polycondensation reaction on various monomer concentrations for 1,3-PDA-Benzoyl-L-Glu are summarized in **Table 1** and those for 1,4-PDA-Benzoyl-L-Glu in **Table 2**. From tables, the suitable monomer concentrations for the preparation of those two types of polyamide were determined to be 4.00×10^{-1} mol dm^{-3}.

3.2. Thermal Properties

Figure 4 shows thermogravimetric analysis (TGA) thermographs for the present polyamides. The change of diamine component from DADPM to 1,3-PDA or 1,4-PDA led to enhance thermal stability. The degradation temperatures for the present polyamides were over 285˚C, whereas that for DADPM-Benzoyl-L-Glu to be 155.7˚C. The adoption of diamine component of 1,3-PDA or 1,4-PDA instead of DADPM might make obtained polyamides less flexible. As a result, the thermal stability of the present polyamides was enhanced [23].

Figure 5 displays DSC thermographs of the polyamides. The glass transition temperatures were determined

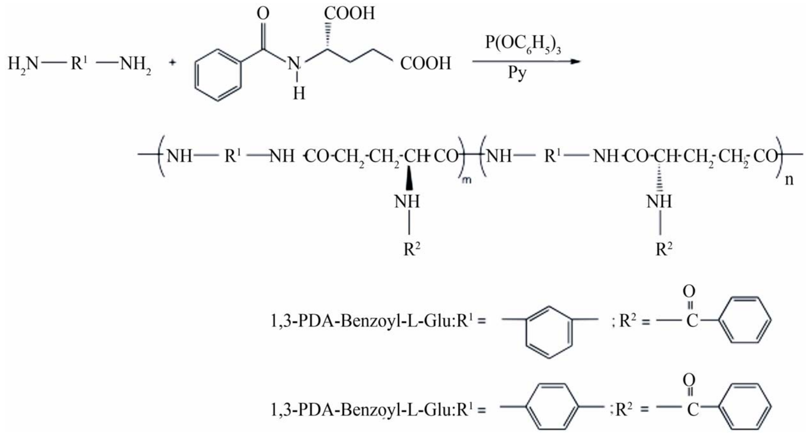


Figure 1. Synthetic scheme of chiral polyamides.

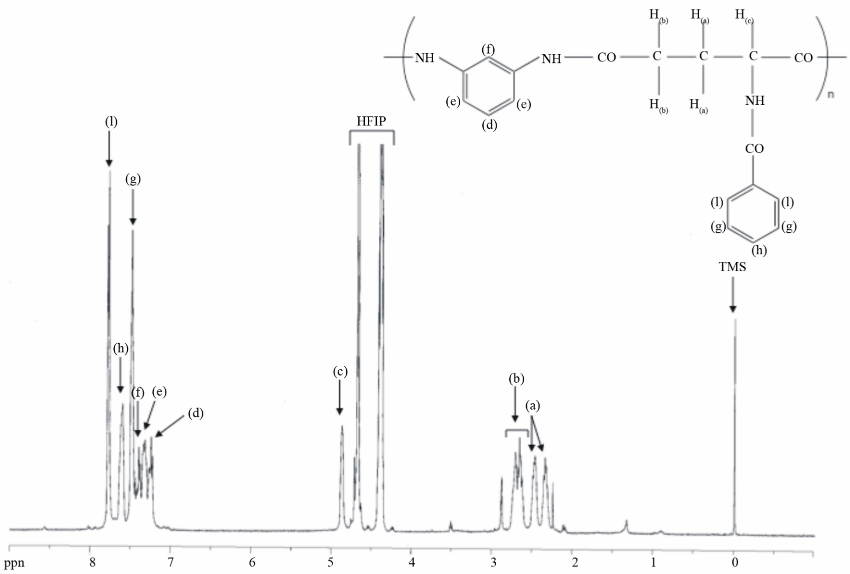


Figure 2. ^{1}H-NMR spectrum of polyamide from 1,3-PDA and Benzoy-L-Glu-OH (500 MHz, HFIP-d_2).

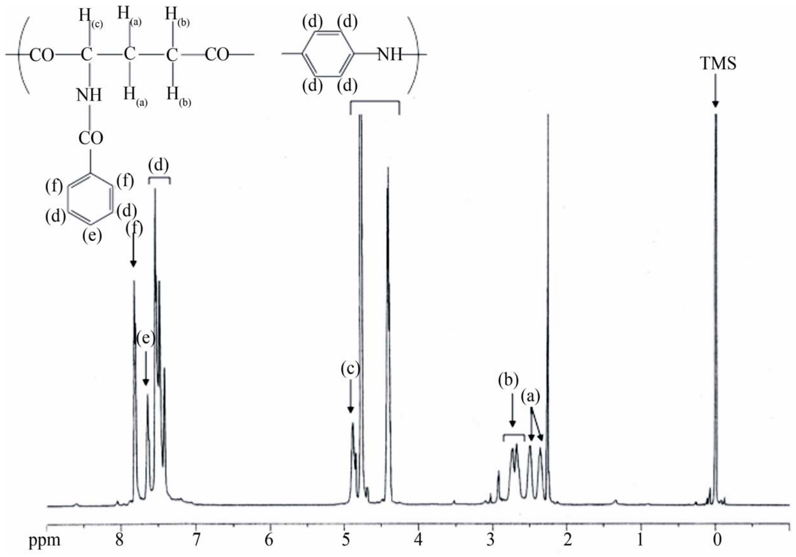
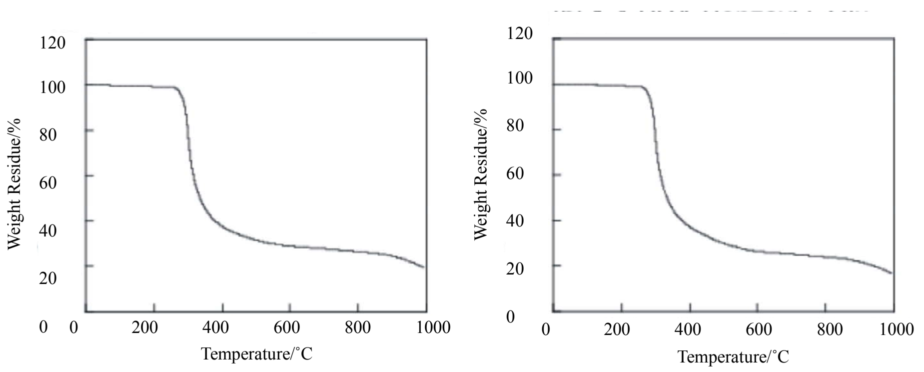
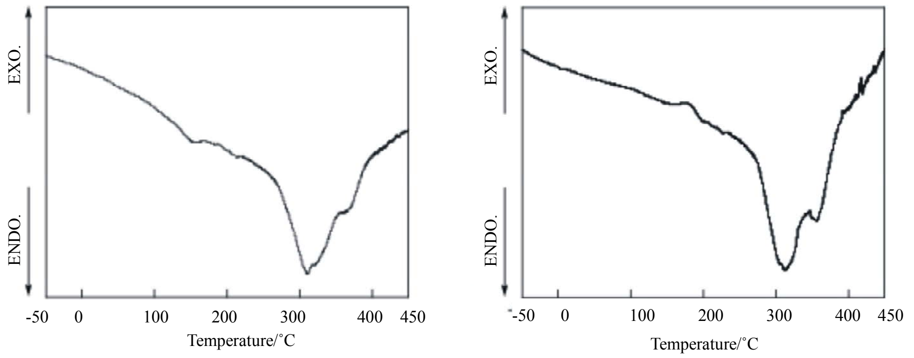


Figure 3. ^{1}H-NMR spectrum of polyamide from 1,4-PDA and Benzoy-L-Glu-OH (500 MHz, HFIP-d_2).



(a) (b)

Figure 4. TGA curves of chiral polyamides consisting of glutamyl residue as a diacid component. (Heating rate, 10˚C·min^{-1}.); (a) 1,2-PDA-Benzoyl-L-Glu; (b) 1,4-PDA-Benzoyl-L-Glu.



(a) (b)

Figure 5. DSC curves of chiral polyamides consisting of glutamyl residue as a diacid component. (Heating rate, 20˚C min^{-1}; N_2 flow, 50 cm^3 min^{-1}.); (a) 1,3-PDA-Benzoyl-L-Glu; (b) 1,4-PDA-Benzoyl-L-Glu.

Table 1. Polycondensation reaction of 1,3-phenylendiamine (1,3-PDA) and Benzoyl-L-Glu-OH by means of triphenyl phosphite[a].

Exp.	Monomer Conc.[b]	PDA	Benzoyl-L-Glu-OH	Triphenyl Phosphite	NMP/Py	LiCl	Yield	η_{inch}[c]
No.	mol·dm^{-3}	G (mol)	G (mol)	G (mol)	cm^3/cm^3	g	g (%)	g^{-1} cm^3
1	3.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8626 (6.003×10^{-3})	8/2	0.400	0.823 (84.8)	60
3	4.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8621 (6.001×10^{-3})	6/1.5	0.300	0.795 (81.9)	83
3	5.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8628 (6.004×10^{-3})	4.8/1.2	0.240	0.812 (83.7)	56

[a]Polymerization temp., 80˚C; polymerization time, 3 h; [b]Monomer Conc. = $[1,3\text{-PDA}]_0 = [\text{Benzoyl-L-Glu-OH}]_0$; [c]Measured at a concentration of 5.0 × 10 – 3 g cm^{-3} in HFIP at 25˚C.

to be 152.7˚C for 1,3-PDA-Benzoyl-L-Glu and 155.2˚C for 1,4-PDA-Benzoyl-L-Glu, respectively, whereas that for DADPM-Benzoyl-L-Glu to be 91.4˚C [13]. The drastic increment of glass transition temperature is also due to the adoption of more rigid diamine monomer of 1,3-PDA or 1,4-PDA instead of DADPM.

3.3. Mechanical Properties

Mechanical properties of the present polyamides were studied. The strain-stress curves of those membranes are given in **Figure 6**. Mechanical properties for the present membranes are summarized in **Table 3** together with common polymers [24].

3.4. Chiroptical Properties

The optical rotations ($[\alpha]_D$) of two types of chiral polyamide are summarized in **Table 4**, together with that of the corresponding diacid monomer, Benzoyl-L-Glu-OH. The results in **Table 4** revealed that optically active polyamides were successfully prepared *via* polycondensation reaction activated by TPP. Those polyamides were expected to show chiral recognition ability from the facts

Table 2. Polycondensation reaction of 1,4-phenylendiamine (1,4-PDA) and Benzoyl-L-Glu-OH by means of triphenyl phosphite[a].

Exp. No.	Monomer Conc.[b] mol dm^{-3}	PDA g (mol)	Benzoyl-L-Glu-OH g (mol)	Triphenyl Phosphite g (mol)	NMP/Py cm^3/cm^3	LiCl g	Yield g (%)	η_{inch}[c] g^{-1} cm^3
21	3.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8617 (6.000×10^{-3})	8/2	0.400	0.883 (91.0)	62
22	4.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8621 (6.001×10^{-3})	6/1.5	0.300	0.891 (91.8)	64
23	5.00×10^{-1}	0.3245 (3.000×10^{-3})	0.7538 (3.000×10^{-3})	1.8621 (6.001×10^{-3})	4.8/1.2	0.240	0.899 (92.7)	56

[a]Polymerization temp., 80˚C; polymerization time, 3 h; [b]Monomer Conc. = [1,4-PDA]$_0$ = [Benzoyl-L-Glu-OH]$_0$; [c]Measured at a concentration of 5.0 × 10 – 3 g cm-3 in HFIP at 25˚C.

Table 3. Ultimate mechanical properties of chiral polyamides.

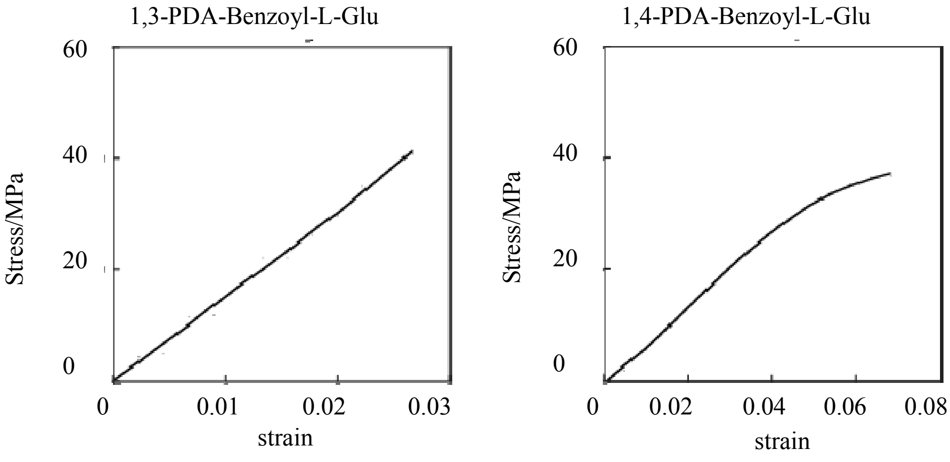
Membrane (Film)	Tensile strength at break/MPa	Elongation at break/%	Tensile modulus/ GPa
1,3-PDA-Benzoyl-L-Glu	37	2.7	1.4
1,4-PDA-Benzoyl-L-Glu	36	6.4	0.73
Polystyrene[a]	50	2.5	3.4
Poly(methyl methacrylate)[a]	65	10.0	3.2
Nylon 66[a]	80	200.0	2.0
Nylon 6[a]	75	300.0	1.9

[a]Cited from ref. 24.

Table 4. Specific rotations of diacid monomers and chiral polyamides.

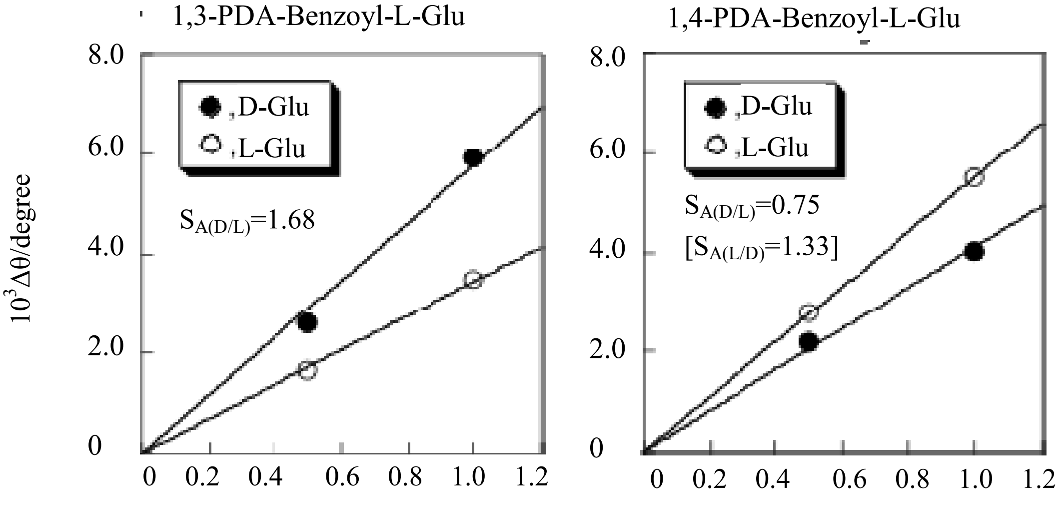
	$[\alpha]_D$
	deg cm^2 g^{-1}
Benzoyl-L-Glu-OH[a]	14.2
1,3-PDA-Benzoyl-L-Glu[b]	3.7
1,4-PDA-Benzoyl-L-Glu[b]	9.7

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



(a) (b)

Figure 6. Strain-stress curves of chiral polymaides consisting of Benzoyl-L-Glu as a diacid component.



(a) (b)

Figure 7. Adsorption isotherms of D-Glu and L-Glu on the chiral polyamide films at 27˚C.

that there can be found asymmetric environments in those polyamides.

3.5. Adsorption Selectivity

As described in the last part in the previous section, those polyamides were expected to show chiral recognition ability. To this end, chiral recognition ability of those two types of polyamide was studied by surface plasmon resonance (SPR) spectroscopy. Compared with usual adsorption experiments for adsorption selectivity, SPR spectroscopy provides a rapid and facile evaluation method. The observed shift in the incidence angle (Δθ) was plotted as a function of the substrate concentration and shown in **Figure 7**. Apparent adsorption isotherms of D-Glu and L-Glu for those two types of polyamide gave straight lines passing through origin, implying that both D-Glu and L-Glu were non-specifically adsorbed on those chiral polyamide films. The experiment for selective adsorption of D-Glu and L-Glu from racemic mixture of Glu cannot be conducted by SPR spectroscopy. The adsorption selectivity was calculated by the following Equation [24]:

$$S_{A(\mathrm{i/j})} = \Delta\theta_{\mathrm{i}} / \Delta\theta_{\mathrm{j}}$$

The subscripts D and L refer to the D-isomer and the L-isomer of Glu, respectively. There are two situations; i = D, j = L and i = L, j = D.

As can be seen in **Figure 7**, 1,3-PDA-Benzoyl-L-Glu adsorbed D-Glu in preference to L-Glu and the adsorption selectivity toward D-Glu was determined to be 1.68. Contrary to this, L-Glu was preferentially incorporated into 1,4-PDA-Benzoyl-L-Glu and the adsorption selectivity toward L-Glu was determined to be 1.33. In the previous study, DADPM-Benzoyl-L-Glu showed adsorption selectivity toward D-Glu and the adsorption selectivity toward the D-isomer was determined to be 1.64 [13]. Even though 1,4-PDA-Benzoyl-L-Glu was prepared from same diacid component of Benzoyl-L-Glu-OH, it showed the opposite adsorption selectivity. This difference might be due to the fact that 1,4-PDA-Benzoyl-L-Glu consisted of 1,4-PDA as a diamine component.

From the results of adsorption study, the present chiarl polyamides are expected to show chiral separation ability as a form of membrane, adsorbent, stationary phase, and so forth.

4. Conclusion

Polyamides with chiral environment were obtained from aromatic diamine, 1,3-phenylenediamine (1,3-PDA) or 1,4-phenylenediamine (1,4-PDA), and N-α-benzoyl-L-glutamic acid (Benzoyl-L-Glu). The optical rotation ($[\alpha]_D$) for 1,3-PDA-Benzoyl-L-Glu was determined to be 3.7 deg cm^2 g^{-1}, while that for 1,4-PDA-Benzoyl-L-Glu to be 9.7 deg cm^2 g^{-1}. 1,3-PDA-Benzoyl-L-Glu showed adsorption selectivity toward D-Glu and its adsorption selectivity was determined to be 1.68. Contrary to this, 1,4-PDA-Benzoyl-L-Glu showed adsorption selectivity toward L-Glu and the adsorption selectivity toward L-Glu was determined to be 1.33. From those results, those two types of chiral polyamide are expected to applicable to chiral separation or chiral recognition.

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