Optically Active Polymers Derived from Chiral 2-Oxazoline. Synthesis, Characterization, and Chiroptical Properties

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ABSTRACT: A new monomer (1*S*,2*S*)-(+)-2-acetamido-1-phenyl-1,3-propanediol (**4**) was synthesized *via* the hydrolysis of (4*S*,5*S*)-(−)-4-hydroxymethyl-5-phenyl-2-oxazoline (**2**), obtained from (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol (**1**) and ethyl orthoacetate. Optically active polyurethanes (PU) with reduced viscosity of 0.15 and 0.13 g dl^{-1} were prepared by polyaddition reaction of the diol **4** with 4,4′-diphenylmethane diisocyanate (MDI) and toluene-2,4-diisocyanate (TDI), respectively. Optically active polyester was prepared by polycondensation reaction with isophthaloyl chloride. The chiroptical properties of these optically active monomers and polymers, in solution or film state, were investigated by circular dichroic spectra (CD).

    KEY WORDS   Optically Active Polymers / 2-Oxazoline / Hydrolysis / (1*S*,2*S*)-(+)-2-Acetamido-1-phenyl-1,3-propanediol / Polyurethanes / Polyester / Circular Dichroic Spectra /

There exist many optically active (chiral) polymers. For example, starches and celluloses are the indispensable resources of life; enzymes and nucleic acids are the catalytic and hereditary substances, respectively, in biochemical processes. In order to mimic and throw light on the sophisticated functions played by natural polymers, a lot of optically active polymers have been synthesized, and the relation between structures, properties, and functions, as well as applications have been investigated.[1] The important applications of optically active polymers are mainly as catalysts for asymmetric synthesis[2,3] and as chiral stationary phases (CSP) for the direct optical resolution of enantiomers.[4,5] It has been found that certain optically active polymers can be absorbed on macroporous silica gels and used as effective packing materials for direct optical resolution of enantiomers by high-performance liquid chromatography (HPLC).[5] In polymeric chiral stationary phases, highly ordered conforma-

tion plays important roles in chiral recognition as well as the simultaneous interactions between functional groups.[4]

According to the starting monomers, optically active polymers have been synthesized from polymerization of chiral monomers, stereoelective polymerization of racemic monomers, and asymmetric polymerization of achiral monomers.[1] However, the surest method for the preparation of optically active polymers is the polymerization of chiral monomers. Optically active polyurethanes, polyamides, and polyesters are well known in this category. Chiral monomers are usually obtained by asymmetric synthesis or by optical resolution of racemates. Cationic ring-opening polymerization of 4- or 4,5-substituted chiral 2-oxazolines have been reported by Saegusa *et al.*[6,7] However, molecular weight was only several thousands because the substituted groups hinder the electrophilic attack by oxazolinium.[8] (4*S*,5*S*)-(−)-2-Alkyl-4-hydroxymethyl-5-phenyl-2-oxazoline is a

versatile chiral template and has been used in asymmetric synthesis for the preparation of various chiral compounds.[9,10] In addition, 2-oxazolines are easily hydrolyzed under acidic conditions to obtain ring-opened derivatives.[10-13]

The objective of this work is to synthesize and characterize the optically active polyurethanes and polyester from (1S,2S)-(+)-2-acetamido-1-phenyl-1,3-propanediol (**4**) which has not been reported so far. Monomer **4** is synthesized by the hydrolysis of (4S,5S)-(−)-4-hydroxymethyl-5-phenyl-2-oxazoline (**2**) which is obtained from (1S,2S)-(+)-phenyl-2-amino-1,3-propanediol (**1**) and ethyl orthoacetate. Chiroptical properties of the monomers and polymers, in solution or film-state, are investigated using circular dichroic spectra (CD).

EXPERIMENTAL

Chemicals

(1S,2S)-(+)-1-Phenyl-2-amino-1,3-propanediol (**1**) and triethyl orthoacetate were purchased from Aldrich and Tokyo Chemical Co., respectively, and used without further purification. 4,4′-Diphenylmethane diisocyanate (MDI) was refluxed in *n*-hexane and hot-filtered to remove insoluble components. The precipitates in the filtrate were collected and dried *in vacuo* overnight. Toluene-2,4-diisocyanate (TDI) and phenyl isocyanate were pure reagents and vacuum distilled before reaction. Isophthaloyl chloride (Merck) was pure reagent and used as received. Chloroform and 1,2-dichloroethane were refluxed with calcium hydride and then distilled before use. Other reagents and solvents were pure reagents and all used as received.

Measurements

Infrared spectra (IR) were recorded using an IR spectrophotometer, model IR-810 from Japan Spectroscopic Co, at a resolution of 4 cm^{-1}. Melting points were determined on a Fargo MP-1D and are uncorrected. ^{1}H NMR spectra were recorded using a Brucker 100 MHz spectrometer. Optical rotations were measured using a Jasco DIP-360 digital polarimeter at 25°C. The reduced viscosity of polymers was measured at 30°C using an Ostwald viscometer, the concentration was about 0.15 g dl^{-1} in *N,N*-dimethylformamide (DMF). The molecular weight of polyester was measured with a GPC equipped with three Shimadzu columns (Shimpack, #801, 8025, 804). A Shimadzu RID-6A detector was calibrated with monodisperse polystyrene standards from Du Pont. The flow rate was 1.0 ml min^{-1} tetrahydrofuran (THF) at 40± 0.1°C.

The circular dichroic (CD) and UV spectra of monomers and polymers were measured at room temperature on a Jasco J-720 spectropolarimeter. Concentration was 0.15 repeating-unit-mol l^{-1} (or mol l^{-1}) for polymers (or monomers). All CD spectra were given in molecular circular dichroism, with cm^2/repeating-unit-mmol (or cm^2 mmol^{-1}) unit, which was calculated by the following equation:

$$\Delta\varepsilon = [\theta]/3300 \quad \text{and} \quad \theta = 0.1 \times [\theta] \times m/M_w$$

where M_w is the repeating-unit molecular weight (or molecular weight) of the polymers (or low molecular weight compounds); m is the sample weight per unit area (g cm^{-2}); θ is the measured ellipticity (deg) and $[\theta]$ is the molecular ellipticity (deg·cm^2/decimol^{-1}).

The thin films for CD measurement were prepared by casting their solutions (*ca.* 0.1 g ml^{-1} in DMAc) on the outside surface of a quartz cell. The coated films were dried at ambient air and then *in vacuo* for 24 h at room temperature. Each CD measurement was repeated 4 times by rotating the sample cell by 60, 120, 180 degrees from the first position around the axis of the incident light beam to ascertain the absence of linear dichroism.

Synthesis of **2**, **3**, *and monomer* **4** (*Scheme* 1)

(4S,5S)-(−)-4-Hydroxymethyl-5-phenyl-2-

oxazoline (**2**). Into 50 ml of 1,2-dichloroethane were added 10 g of (1*S*,2*S*)-(+)-2-amino-1-phenyl-1,3-propanediol (**1**) and 11.66 g of ethyl orthoacetate, and the mixture was refluxed for 12 h. The oils obtained after evaporation of the solvent were dissolved in ethyl ether and cooled to −40°C. The needle crystals were collected and redissolved in ethyl ether, treated with activated carbon. Recrystallized in ethyl ether to obtain about 5.5 g of **2**. Yield 50%, mp 62—63°C (lit. 64—65°C)[14], $[\alpha]_D^{25} = -155.9°$ (0.1 g dl^{-1}, CHCl$_3$) [lit. −174.6° (1.0 g dl^{-1}, CHCl$_3$)][14]. IR (KBr) v 3200 cm^{-1} (OH), 3000—2800 cm^{-1} (CH$_3$), 1670 cm^{-1} (C=N), 1060 cm^{-1} (C–O–C), 800—700 cm^{-1} (C$_6$H$_5$); ^{1}H NMR (C$_5$D$_5$N) δ 7.3 (m, 5H, C$_6$H$_5$), 5.3 (d, 1H, C$\underline{H}$C$_6$H$_5$), 4.0—3.6 (m, 4H, C$\underline{H}$C$\underline{H_2}$O$\underline{H}$), 2.1 (d, 3H, C$\underline{H_3}$). *Anal.* Calcd for C$_{11}$H$_{13}$NO$_2$: C, 69.09%; H, 6.85%; N, 7.32%. Found: C, 68.78%; H, 6.86%; N, 7.29%.

Into 25 ml of 3 *N* HCl aqueous solution were added 5 g of **2** and stirred at room temperature for 7 h. The precipitates were filtered and dried *in vacuo* to obtain 4.5 g of **3**. IR (KBr) v 3400—3350 cm^{-1} (OH), 3100—3000 cm^{-1} (NH$_3^+$), 3000—2800 cm^{-1} (CH$_3$), 1740 cm^{-1} (CH$_3$$\underline{C}$=O), 1590 cm^{-1} and 1480 cm^{-1} (NH$_3^+$), 1240 cm^{-1} (O=$\underline{C}$–O–C), 800—700 cm^{-1} (C$_6$H$_5$). ^{1}H NMR (DMSO-d_6) δ 8.4 (s, 3H, N$\underline{H_3}^+$), 7.4 (m, 5H, C$_6$H$_5$), 5.7 (d, 1H, C$\underline{H}$C$_6$H$_5$), 3.5—3.1 (m, 4H, C$\underline{H}$C$\underline{H_2}$O$\underline{H}$), and 2.1 ppm (s, 3H, C$\underline{H_3}$).

(*1S*,*2S*)-(+)-2-*Acetamido-1-phenyl-1,3-propanediol* (**4**). The precipitates obtained above were neutralized with aqueous sodium bicarbonate, dissolved and new precipitates appeared after several hours. These materials were collected and recrystallized in distilled water to obtain **4** with yield of 45%. mp 62—63°C, $[\alpha]_D^{25} = +24.9°$ (0.1 g dl^{-1}, CH$_3$OH). IR (KBr) v 3600—3400 cm^{-1} (OH), 3300—3100 cm^{-1} (NHCO), 3000—2800 cm^{-1} (CH$_3$), 1680 cm^{-1} (NH$\underline{CO}$), 1660—1540 cm^{-1} (N$\underline{H}$CO), 800—700 cm^{-1} (C$_6$H$_5$). ^{1}H NMR (DMSO-d_6) δ 7.5—7.2 (m, 6H, $\underline{H}$OCHC$_6$$\underline{H_5}$),

5.4 (d, 1H, C$\underline{H}$C$_6$H$_5$), 4.9—4.7 (m, 2H, CHC$\underline{H_2}$OH), and 3.9—3.8 ppm (m, 1H, C$\underline{H}$CH$_2$OH), 1.7 (s, 3H, C$\underline{H_3}$). *Anal.* Calcd for C$_{11}$H$_{15}$NO$_3$·H$_2$O: C, 58.14%; H, 7.54%; N, 6.16%. Found: C, 58.19%; H, 7.56%; N, 6.21%.

Preparation of Optically Active Polymers (**6a**, **6b**, *and* **7**)

Polyurethane **6a** *from* **4** *and MDI.* To a solution of MDI (2.484 g, 9.93 mmol) in chloroform (20 ml) were added **4** (1.880 g, 9.02 mmol), and the mixture was reacted at 75°C for 24 h. Transparent solids appeared on the inside wall of the reactor after 4 h. The solids obtained after evaporation of the solvent were dissolved in DMF and precipitated in distilled water to obtain 3.49 g of **6a**. Yield 80%, reduced viscosity $[\eta_{sp}/c] = 0.15$ dl g^{-1}, $[\alpha]_D^{25} = -24.6°$ (0.1 g dl^{-1}, DMF). IR (KBr) v 3600—3200 cm^{-1} ($\underline{\text{NHCO}}$, $\underline{\text{NHCOO}}$), 1710 cm^{-1} (NH$\underline{\text{COO}}$), 1650 cm^{-1} (NH$\underline{\text{CO}}$), 1600 cm^{-1} (C$_6$H$_6$), 1520 cm^{-1} ($\underline{\text{NHCO}}$), 1420 cm^{-1} (C$_6$H$_6$), 1220 cm^{-1} ($\underline{\text{C–O–C}}$=O), 1060 cm^{-1} (H$\underline{\text{N–C}}$=O, HN–$\underline{\text{COO}}$), 800—700 cm^{-1} (C$_6$H$_6$). ^{1}H NMR (DMSO-d_6) δ 9.6—9.5 (d, 2H, N$\underline{H}$COO), 7.4—7.1 (m, 13H, CHC$_6$$\underline{H_5}$, OOCHNC$_6$$\underline{H_4}CH_2C_6$$\underline{H_4}$NHCOO), 5.7 (d, 1H, C$\underline{H}C_6H_5$), 4.3—4.2 (m, 2H, C$\underline{H_2}$OC=O), 3.7 (m, 3H, C$\underline{H}$NHCO, C$_6H_4C\underline{H_2}C_6H_4$), and 1.8—1.7 ppm (d, 3H, C$\underline{H_3}$). *Anal.* Calcd for (C$_{26}$H$_{25}$N$_3$O$_5$)$_n$: C, 67.96%; H, 5.48%; N, 9.14%. Found: C, 67.67%; H, 5.61%; N, 8.86%.

Polyurethane **6b** *from* **4** *and TDI.* The polyaddition reaction of **4** with TDI was similar to that with MDI except that the reaction time was extended to 48 h. The polymer was isolated as described in the synthesis of **6a**. Yield 70%, reduced viscosity $[\eta_{sp}/c] = 0.13$ dl g^{-1}, $[\alpha]_D^{25} = -20.6°$ (0.1 g dl^{-1}, DMF). IR (KBr) v 3600—3200 cm^{-1} ($\underline{\text{NHCO}}$, $\underline{\text{NHCOO}}$), 1710 cm^{-1} (NH$\underline{\text{COO}}$), 1650 cm^{-1} (NH$\underline{\text{CO}}$), 1600 cm^{-1} (C$_6$H$_6$), 1530 cm^{-1} ($\underline{\text{NHCO}}$), 1410 cm^{-1} (C$_6$H$_6$), 1230 cm^{-1} (C–O–C=O), 1060 cm^{-1} (H$\underline{\text{N–C}}$=O, HN–$\underline{\text{COO}}$), 800—700 cm^{-1}

(C_6H_6). ^1H NMR (DMSO-d_6) δ 9.6 (d, 1H, OOCHNC$\underline{H}_3C_6H_3N\underline{H}$COO), 8.9 (S, 1H, OOC$\underline{H}NCH_3C_6H_3$NHCOO), 7.4—7.0 (m, 8H, CHC$_6\underline{H}_5$, OOCHNCH$_3C_6\underline{H}_3$NHCOO), 5.7 (d, 1H, C$\underline{H}$C$_6$H$_5$), 4.2 (m, 2H, C$\underline{H}_2$OC=O), 3.7 (m, 1H, C$\underline{H}$NHCO), 2.2—2.1 (d, 3H, OOCHNC$\underline{H}_3C_6H_3$NHCOO), and 1.8—1.7 ppm (d, 3H, C$\underline{H}_3$CONH). *Anal.* Calcd for (C$_{20}$H$_{21}$N$_3$O$_5$)$_n$: C, 62.65%; H, 5.52%; N, 10.96%. Found: C, 62.32%; H, 5.39%; N, 10.69%.

Polyester 7 from 4 and isophthaloyl chloride. Into 20 ml of chloroform were added 1.992 g (9.83 mmol) of isophthaloyl chloride, 2.054 g (9.82 mmol) of **4**, and 2.388 g (23.6 mmol) of triethylamine. The mixture was reacted at 60°C for 48 h. The solids obtained after evaporation of the solvent were dissolved in DMF and precipitated in distilled water to obtain 2.02 g of **7**. Yield 55%, reduced viscosity [η_{sp}/c] = 0.06 dl g^{-1} ($\bar{M}_n$ = 744 and $\bar{M}_w$ = 4450 by GPC), [α]$_D^{25}$ = −30.8° (0.1 g dl^{-1}, DMF). IR (KBr) v 3400 cm^{-1} (N$\underline{H}$CO), 1730 cm^{-1} (O=C–O), 1660 cm^{-1} (NH$\underline{CO}$), 1540 cm^{-1} (N$\underline{H}$CO), 1230 cm^{-1} (O=$\underline{C}$–O–C), 800—700 cm^{-1} (C$_6$H$_6$). ^1H NMR (DMSO-d_6) δ 8.0—7.0 (m, 9H, CHC$_6\underline{H}_5$, OCOC$_6\underline{H}_4$OCO), 6.1 (m, 1H, C$\underline{H}$C$_6$H$_5$), 4.5—4.4 (m, 3H, C$\underline{H}_2$OC=O, C$\underline{H}$NHCO), and 1.7 ppm (d, 3H, C$\underline{H}_3$CONH).

Preparation of CD Model Compound (5)

Into 10 ml of chloroform were added 1.0 g (4.78 mmol) of **4** and 1.708 g (14.3 mmol) of

phenyl isocyanate and reacted at 75°C for 36 h. The solids obtained after evaporating the solvent were recrystallized in ethyl acetate to give 1.2 g of **5**. Yield 57%, mp 172—173°C, [α]$_D^{25}$ = −38.6° (0.1 g dl^{-1}, DMF). IR (KBr) v 3600—3200 cm^{-1} (N$\underline{H}$CO, N$\underline{H}$COO), 1710 cm^{-1} (NH$\underline{COO}$), 1650 cm^{-1} (NH$\underline{CO}$), 1600 cm^{-1} (C$_6$H$_6$), 1530 cm^{-1} (N$\underline{H}$CO), 1440 cm^{-1} (C$_6$H$_6$), 1220 cm^{-1} (C–O–C=O), 1100—1000 cm^{-1} (H$\underline{N}$–C=O, H$\underline{N}$–COO), 780—680 cm^{-1} (C$_6$H$_6$). ^1H NMR (DMSO-d_6) δ 9.7—9.6 (d, 2H, N$\underline{H}$COO), 7.5—6.9 (m, 15H, CHC$_6\underline{H}_5$, OOCHNC$_6\underline{H}_5$), 5.8 (d, 1H, C$\underline{H}$C$_6$H$_5$), 4.5—4.2 (m, 2H, C$\underline{H}_2$OC=O), 3.8—3.6 (m, 1H, C$\underline{H}$NHCO), and 1.8 ppm (s, 3H, C$\underline{H}_3$). *Anal.* Calcd for C$_{25}$H$_{25}$N$_3$O$_5$: C, 67.10%; H, 5.63%; N, 9.39%. Found: C, 66.92%; H, 5.65%; N, 9.31%.

RESULTS AND DISCUSSION

Preparation of Chiral Monomers

(1S,2S)-(+)-2-Amino-1-phenyl-1,3-propanediol (**1**) contains two hydroxyl groups and one amino group. Direct protection of amino group *via* amide formation with acid chloride was reported by Levy and Boyd *et al.*[8,15] However, it is difficult to obtain pure compounds because the reactive acid chloride easily reacts with both amino and hydroxy groups. Based on this consideration, we protected the amino group of *via* the synthesis and subsequent hydrolysis of (4S,5S)-(−)-4-
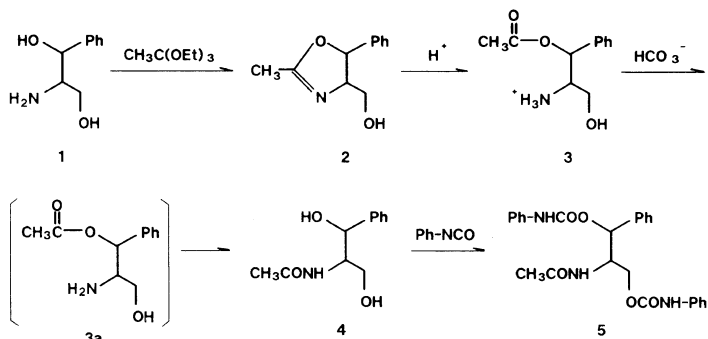
Scheme 1.
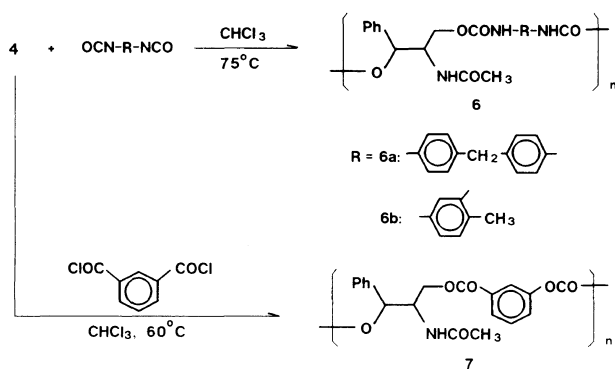
Scheme 2.

hydroxymethyl-5-phenyl-2-oxazoline (**2**) as shown in Scheme 1. Our first consideration was to obtain the ester amine (**3a**) as monomer for the preparation of optically active poly(-urethane-*co*-urea). However, the nucleophilic amino groups in **3a** easily attack the neighboring ester group to generate (1*S*,2*S*)-(+)-2-acetamido-1-phenyl-1,3-propanediol (**4**). The ester amine is the kinetic product and easily transforms to **4** which is the thermodynamic product. The kinetic product (**3a**) can be completely isomerized to the thermodynamic product (**4**) by extending the reaction time or increasing the reaction temperature. From elemental analysis, **4** contains one molecule of crystalline water. The crystalline water is difficult to remove by usual recrystallization methods. Moreover, it is highly hygroscopic and gradually transforms to a viscous liquid after absorbing the moisture in the air. This is the reason why the polymerization always failed if crystalline water of **4** was not completely removed by heating *in vacuo*.

Synthesis of Optically Active Polymers

The polyaddition reaction of diol with diisocyanate is an established method for the synthesis of polyurethanes. Accordingly, (1*S*,2*S*)-(+)-2-acetamido-1-phenyl-1,3-pro-panediol (**4**), which contains two hydroxyl groups, would be an effective monomer for the preparation of optically active polymers

Table I. Specific rotations of monomers and polymers

Monomer or polymer	mp	η_{red}[a]	$[\alpha]_D^{26}$[b]
	°C	dl g^{-1}	Degree
1	111—113[c]	—	+25.5—26.5[d]
2	62—63	—	−155.9
4	62—63	—	+24.9
5	172—173	—	−38.6
6a	—	0.15	−24.6
6b	—	0.13	−20.6
7	—	0.06	−30.8

[a] Measured at *ca.* 0.15 g dl^{-1} in DMF at 30°C.
[b] Measured at 0.1 g dl^{-1} in various solvents (see EXPERIMENTAL section).
[c] Synthesis reagent from Merck.
[d] $[\alpha]_D^{20}$ (2 g dl^{-1}, methanol).

(Scheme 2). As shown in Table I, the reduced viscosity of polyurethane **6a** and **6b** are 0.15 and 0.13 dl g^{-1}, respectively. The viscosity of polyester **7** from isophthaloyl chloride and **4** is only 0.06 dl g^{-1} ($\bar{M}_w$ and $\bar{M}_n$ are 4450 and 744, respectively, as determined by GPC). The steric hindrance of the phenyl group of **4** seems to prevent the addition reaction of isocyanate to hydroxyl groups of **4**. The addition of dibutyltin dilaurate (T-12) as catalyst results in early appearance of solid polymers on the inside wall of the reactor, but the reduced viscosity remains almost unchanged. The low solubility of chloroform to polyurethanes
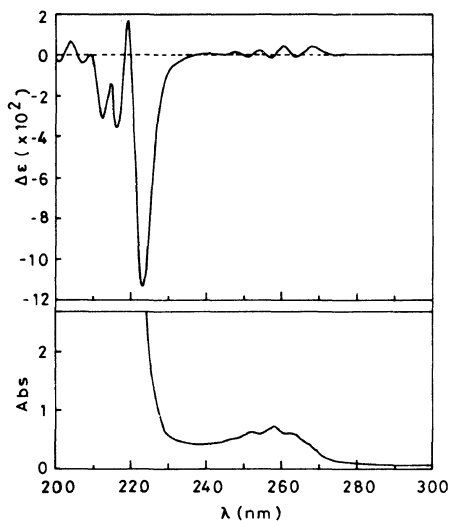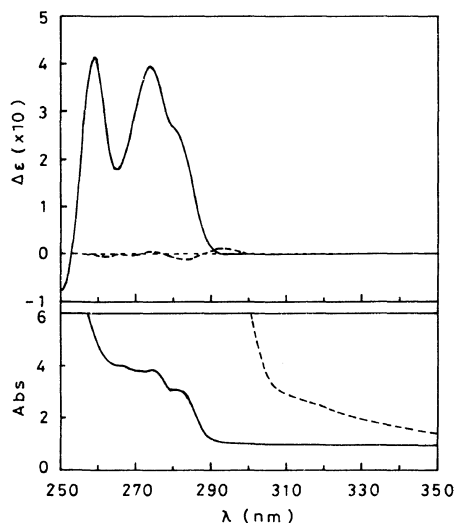
Figure 1. CD and UV spectra of **2** in methanol.

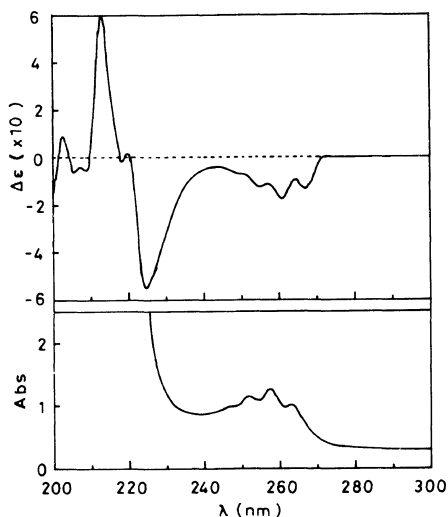**Figure 3.** CD and UV spectra of **6a** (-----) and **5** (——) in DMAc solution.

Figure 2. CD and UV spectra of **4** in methanol.

seems also to prevent the formation of high molecular weight polymers.

CD Spectra of 1, 2, and monomer 4

The CD spectra (with UV spectra) of **2** and **4** in methanol are shown in Figures 1 and 2, respectively. The CD spectra of **1** and **4** exhibit negative bands (negative Cotton effect) at 240—270 nm, which may be assigned to π–π^*

transition of the phenyl chromophores. The CD absorption of **4** ($-0.15 \, cm^2 \, mmol^{-1}$) is more intensive than that of **1** ($-0.014 \, cm^2 \, mmol^{-1}$). The CD bands at 240—270 nm of **2** degenerates significantly, indicating that formation of oxazoline ring weakens the CD bands of aromatic chromophores. The negative CD bands at 223 nm ($-0.115 \, cm^2 \, mmol^{-1}$) of **2** and at 228 nm ($-0.57 \, cm^2 \, mmol^{-1}$) of **4** can be assigned to n–π^* transition of oxazoline rings and amide carbonyl, respectively.

CD Spectra of Model Compound (5)

The CD spectra of **5** in N,N-dimethylacet-amide (DMAc) and film-state are shown in Figures 3 and 4. Their shapes are very similar, although the wavelength range in Figure 3 and the scale in Figure 4 are drawn differently because of the limitation of DMAc solution and ease of comparison, respectively. Comparing the CD spectra of **4** with that of **5**, the negative bands at 240—270 nm of **4** are replaced by positive bands at 250—290 nm in **5**. These new positive bands can be assigned to components of the split π–π^* transition due to an exciton coupling of the phenyl carbamate in **5**.
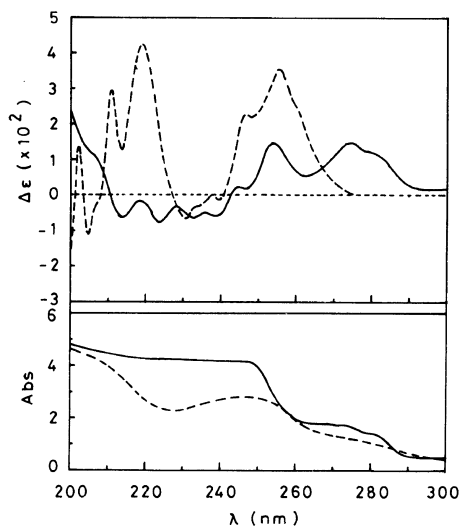
Figure 4. CD and UV spectra of **6a** (----) and **5** (——) in the film state.
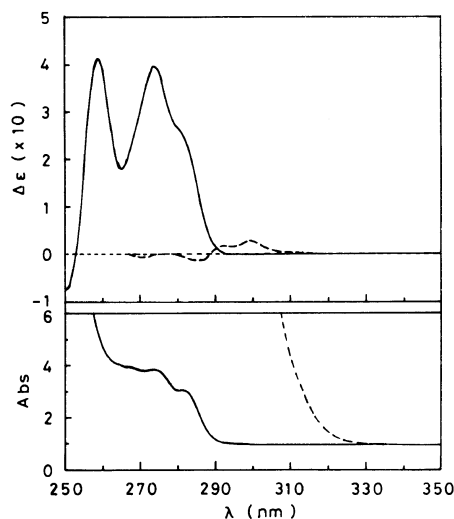

Figure 5. CD and UV spectra of **6b** (----) and **5** (——) in DMAc solution.

Chiroptical Properties of Polymers (6a, 6b, 7)

The chiroptical properties of polymers can be investigated by comparing their CD spectra with those of the corresponding model compounds.[16] In general, the random conformation of a polymer results in weaker Cotton effect at about the same wavelength range than that of the corresponding model compound. However, the appearance of a new CD band or stronger intensity than that of the corresponding model compound can be attributed to the formation of some kind of highly ordered conformation. In this study, the Cotton effects of urethane carbonyl and aromatic chromophores are mainly investigated.

The CD and UV spectra of **6a** and **5** in DMAc are shown in Figure 3. The CD spectrum of **6a** shows very small $\Delta\varepsilon$ comparing to that of model compound (**5**). This CD result suggests that **6a** exists in random conformation in DMAc. In the film state, the CD spectrum of **6a** does not exhibit band at 274 nm as **5** (Figure 4). However, two large new bands appear at 219 nm (+ 0.043 cm²/repeating-unit-mmol) and 210 nm (+ 0.03 cm²/repeating-unit-mmol), which are opposite to those of **5**.
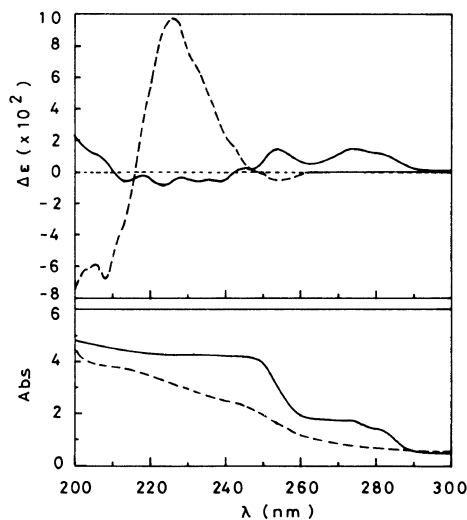

Figure 6. CD and UV spectra of **6b** (----) and **5** (——) in the film state.

Moreover, the positive bands between 240 and 272 nm are more intense than those of **5**. These CD results suggest strongly that **6a** forms an ordered conformation in the film state.[17] This ordered conformation would be caused by the strong hydrogen-bonding formed inter- or intramolecularly. The CD spectra of **6b** with that of **5** in DMAc and film state are shown in
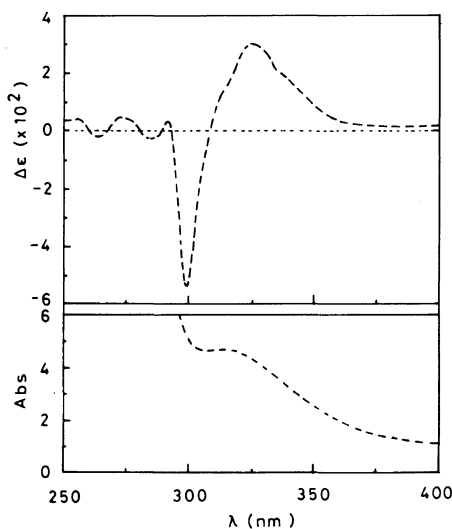
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Figure 7. CD and UV spectra of **7** in DMAc solution.

Figures 5 and 6, respectively. In DMAc solution, **6b** also exhibits very small molecular circular dichroism ($\Delta\varepsilon$). Therefore, **6b** also exists in random conformation in DMAc solution. However, in the film state, **6b** shows a very large positive band at 226 nm (+0.098 cm²/repeating-unit-mmol), although the CD bands at 254 and 274 nm of **5** are not observed. **6b** may exist in an ordered conformation in the film state due to hydrogen-bonding formation. Unfortunately, these ordered conformations of **6a** and **6b** in the film state cannot be currently specified.

The CD spectrum of polyester **7** in DMAc is shown in Figure 7. In DMAc **7** shows a positive band at 325 nm (+0.03 cm²/repeating-unit-mmol) and a negative band at 300 nm (−0.055 cm²/repeating-unit-mmol), but in the film state it only shows a negative one at 265 nm (−0.048 cm²/repeating-unit-mmol). However, it is not easy to study its conformation because high molecular weight samples can not be obtained.

CONCLUSION

A new optically active monomer (1*S*,2*S*)-

(+)-2-acetamido-1-phenyl-1,3-propanediol (**4**) was successfully synthesized *via* the hydrolysis of (4*S*,5*S*)-(−)-4-hydroxymethyl-5-phenyl-2-oxazoline (**2**). Optically active polyurethanes were prepared by polyaddition reaction of **4** with MDI and TDI, respectively. The reduced viscosity was between 0.13 and 0.15 dl g⁻¹. Their model compound was prepared by reaction of **4** with excess of phenyl isocyanate. Polyester was obtained by polycondensation of **4** with isophthaloyl chloride. However, the molecular weight was very low ($\bar{M}_w$=4450, $\bar{M}_n$=744). Comparison of the CD spectra of polyurethanes with those of model compound (**5**) suggests that **6a** and **6b** exist in random confomation in DMAc solution, but form as ordered conformations in the film state. The chiroptical properties of polyester **7** are not conclusive due to its low molecular weight.

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