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Polycondensation of Chiral 3,4-Dihydro-*N*-Substituted Succinimide and Phthalic Acid Dichloride

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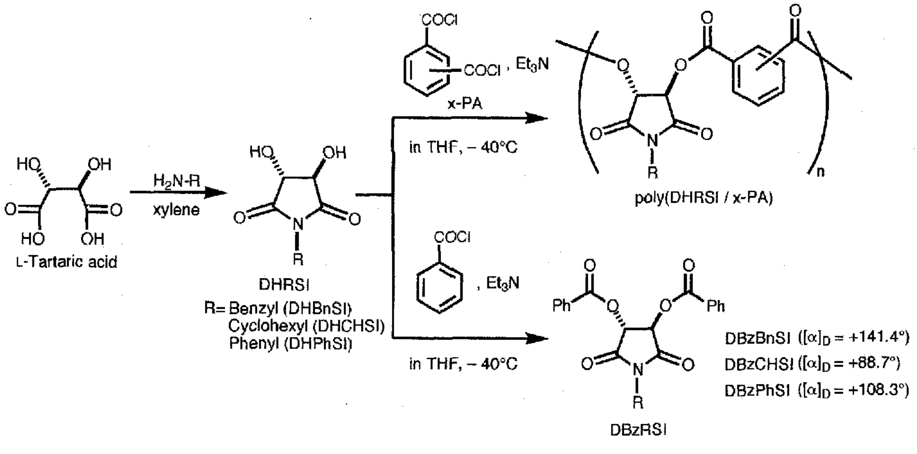
Summary

Polycondensations of (*3R,4R*)-3,4-dihydro-*N*-substituted succinimide (DHRSI) and phthaloyl dichloride (*x*-PA) were carried out to obtain optically active polyesters ($[\alpha]_D$ = -11.0° to +206.1°). The GPC curve of poly(DHPhSI/*o*-PA) by polarimetric detector (α_{Hg}) showed *dextro* rotation at a low molecular weight fraction and *levo* rotation at a high molecular weight fraction. Optical activities were attributed to configurational and/or conformational chirality.

Introduction

Optically active polyesters [1], polycarbonate [2], polyamides [3], and polyurethane [4] having chiral carbons in backbones have been synthesized. Several examples of the polymers obtained by polycondensation have been reported to investigate conformation and physical properties of polymers [1d, 1c, 3b]. Recently, we have reported asymmetric anionic polymerization of *N*-substituted maleimide (RMI) initiated by chiral ligand-organometal [5]. The polymerizations of RMI proceed via stereoregularity of *trans* addition to give 3,4-*trans*-succinimide. Chiroptical properties of poly(RMI) could be attributed to the excess of chiral stereogenic centers (*3S,4S*) or (*3R,4R*). (*3R,4R*)-3,4-Dihydro-*N*-substituted succinimide (DHRSI) having *trans* diol structure was easily prepared from L-tartaric acid and amine [6]. In this paper, we report the polycondensation between chiral DHRSI and aromatic diacid chlorides in the presence of triethylamine.



Scheme 1. Polycondensation of Chiral 3,4-Dihydro-*N*-Substituted Succinimide and Phthalic Acid Dichloride

Experimental

Reagents and Solvents

Commercially available L-tartaric acid was used without further purification. Xylene and tetrahydrofuran (THF) were purified by usual methods. Aniline, benzylamine, *tert*-butylamine and triethylamine were purified by distillation. Phthalic acid dichloride and benzoyl chloride were purchased and purified by distillation just before use.

DHRSI

DHRSI was prepared from L-tartaric acid and primary amine by a method of succinimide synthesis reported lately [6].

(3*R*,4*R*)-(+)-3,4-Dihydro-*N*-benzylsuccinimide (DHBnSI)

A dry, 1 L, three-necked, round-bottomed flask is equipped with a magnetic stirrer, Dean-Stark trap, a dropping funnel, and reflux condenser. The flask is charged with 500 mL of xylene and L-tartaric acid (19.0 g, 127 mmol). To the refluxing suspension was added benzylamine (16.5 g, 154 mmol) in a period of 30 min and then reflux was continued for 3 h. The reaction mixture was cooled in an ice and the crystalline was filtered. After being washed twice with cold benzene. The product was recrystallized from water to give the DHBnSI.

Yield: 50%, Colorless needles, mp.: 196-198 °C, (Lit. [6], mp. 196-198 °C), $[\alpha]_{435}$= +321.4°, *c* =1.0 g/dl, *l*=10 cm in THF. ^{1}H-NMR (δ in ppm from TMS in DMSO-d_6) : 4.38 (s, 2H, H-3 and H-4), 4.50-4.61 (m, 2H, CH_2–Ph), 7.23-7.36 (m, 5H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in DMSO-d_6): 41.2 (-CH_2-Ph), 74.4 (C-3 and C-4), 127.5, 127.7, 128.5, 135.9 (aromatic protons), 174.6 (C=O).

(3*R*,4*R*)-(+)-3,4-Dihydro-*N*-cyclohexylsuccinimide (DHCHSI)

DHCHSI was prepared from L-tartaric acid and cyclohexylamine, according to a method similar to that for DHBnSI.

Yield: 41%, Pale yellow plate, mp.: 171-173 °C, $[\alpha]_{435}$= +296.3° *c* =1.0 g/dl, *l*=10 cm in THF. ^{1}H NMR (δ in ppm from TMS in DMSO-d_6): 1.07-1.99 (m, 10H, cyclohexyl protons), 3.78-3.85 (m, 1H, N-CH), 4.26 (s, 2H, H-3 and H-4). ^{13}C NMR (δ in ppm from TMS in DMSO-d_6): 24.7, 25.1, 28.1, 28.3, 28.8 (cyclohexyl group), 50.2 (N-CH), 74.0 (C-3 and C-4), 174.5 (C=O).

(3*R*,4*R*)-(+)-3,4-Dihydro-*N*-phenylsuccinimide (DHPhSI)

DHPhSI was prepared from L-tartaric acid and aniline, according to a method similar to that for DHBnSI.

Yield: 75 %, Colorless needles, mp.: 184-187 °C, $[\alpha]_{435}$= +330.9° *c* =1.0 g/dl, *l*=10 cm in THF. ^{1}H NMR (δ in ppm from TMS in DMSO-d_6): 4.57 (s, 2H, H-3 and H-4), 7.29-7.53 (m, 5H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in DMSO-d_6): 74.0 (C-3 and C-4), 126.8, 128.2, 128.8, 131.9 (phenyl group), 173.9 (C=O).

Model compounds

(3*R*,4*R*)-(+)-3,4-Dibenzoyloxy-*N*-benzylsuccinimide (DBzBnSI)

A dry Schlenk reaction tube was charged with DHBnSI (0.50 g, 2.3 mmol), triethylamine (1.6 mL, 11 mmol) and THF (30 mL) under an atmosphere of dry nitrogen. To a solution was added portionwise 0.48 g (4.6 mmol) of benzoyl chloride at - 40 °C by means of a syringe. The reaction mixture was stirred for 96 h at - 40 °C, and quenched by adding saturated aq. ammonium chloride. The mixture was extracted with ethyl acetate. The combined organic layer was washed by brine, dried over $MgSO_4$. The residue was chromatographed over silica gel (*n*-hexane/ethyl acetate = 5/1, Rf = 0.11) to give DBzBnSI.

Yield: 63%, white solid, mp.: 110-112°C, $[\alpha]_{435}$= +320.8°, $[\alpha]_D$= +141.4° *c* =1.0 g/dl, *l*=10 cm in THF. ^{1}H NMR (δ in ppm from TMS in $CDCl_3$): 4.77-4.89 (m, 2H, -CH_2-Ph), 5.92 (s, 2H, H-3 and H-4), 7.32-8.11 (m, 15H, aromatic protons), ^{13}C NMR (δ in ppm from TMS in $CDCl_3$) : 43.2((-CH_2-Ph), 73.4 (C-3 and C-4), 128.1, 128.3, 128.4, 128.6, 128.8, 130.2, 133.6, 134.0, 134.6 (phenyl group), 165.5 (O=C-O), 169.1 (N-C=O).

(3*R*,4*R*)-(+)-3,4-Dibenzoyloxy-*N*-cyclohexylsuccinimide (DBzCHSI)

DBzCHSI was prepared from DHCHSI and benzoyl chloride, according to a method similar to that for DBzBnSI.

Yield: 21%, white solid, mp.: 116-118°C, $[\alpha]_{435}$= +205.8°, $[\alpha]_D$= +88.7° *c* =1.0 g/dl, *l*=10 cm in THF. *n*-hexane/ethyl acetate = 5/1, Rf = 0.20. ^{1}H NMR (δ in ppm from TMS in $CDCl_3$): 1.21-2.26 (m, 10H, cyclohexyl protons), 4.07-4.19 (m, 1H, N-CH), 5.83 (s, 2H, H-3 and H-4), 7.44-8.10 (m, 10H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$): 24.9, 25.7, 28.5, 29.0 (cyclohexyl group), 52.8 (N-CH), 73.2 (C-3 and C-4), 128.2, 128.6, 130.2, 134.0 (phenyl group), 165.6 (O=C-O), 169.3 (N-C=O).

(3*R*,4*R*)-(+)-3,4-Dibenzoyloxy-*N*-phenylsuccinimide (DBzPhSI)

DBzPhSI was prepared from DHPhSI and benzoyl chloride, according to a method similar to that for DBzBnSI.

Yield: 84%, white solid, mp.: 175-178°C, $[\alpha]_{435}$= +245.0°, $[\alpha]_D$= +108.3° *c* =1.0 g/dl, *l*=10 cm in THF. *n*-

hexane/ethyl acetate = 5/1, Rf = 0.10. ^{1}H NMR (δ in ppm from TMS in $CDCl_3$): 6.00 (s, 2H, H-3 and H-4), 7.41-8.13 (m, 15H, aromatic protons). ^{13}C NMR (δ in ppm from TMS in $CDCl_3$): 73.6 (C-3 and C-4), 126.3, 128.0, 128.6, 129.2, 129.3, 130.2, 130.4, 130.9, 134.1 (phenyl group), 165.7 (O=C-O), 168.5(N-C=O).

Polymerization

Typical experimental procedure is as follows: Polycondensation was carried out in a dry Schlenk reaction tube under dry nitrogen. To a mixture of 0.500 g (2.26 mmol) of DHBnSI and 0.76 ml (5.42 mmol) of triethylamine in tetrahydrofuran (10 mL) was added portionwise 0.459 g (2.26 mmol) of phthaloyl dichloride (*o*-PA) at -40 °C. The reaction mixture was stirred for 96 h, and quenched by adding 5 mL of saturated aq. ammonium chloride. The mixture was extracted with ethyl acetate. The combined organic layer was washed by brine, dried over $MgSO_4$. The residue after evaporation of solvent was purified by re-precipitation from THF-methanol or THF - *n*-hexane systems three times, then filtered and dried *in vacuo.*

Measurements

Gel permeation chromatography (GPC) measurement of polymers was accomplished on a LC-10AS (Shimadzu) equipped with a UV detector SPD-A (Shimadzu) and on a polarimetric detector OR-990 (Japan Spectroscopic Co.) using THF as eluent at 50 °C. Four GPC columns HSG-10, 15, 20, 40H (Shimadzu) were connected in series, and molecular weight was calibrated with standard polystyrene. D- and Hg-line specific optical rotations were measured with a JASCO DIP-140 at 25 °C. Circular dichroism (CD) spectra were obtained using a JASCO J-805. Ultraviolet (UV) spectra were obtained with a Shimadzu UV 2200 spectrophotometer. ^{1}H and ^{13}C NMR spectra of monomers and polymers were measured in DMSO-d_6 or chloroform-*d* at room temperature in the presence of tetramethylsilane (TMS) as an internal standard using a JEOL EX-270 (^{1}H, 270 MHz, ^{13}C, 68.7 MHz) spectrometer.

Results and Discussion

Polycondensations of DHRSI (R= benzyl (DHBnSI), cyclohexyl (DHCHSI), phenyl (DHPhSI)) and phthaloyl dichloride (phthaloyl dichloride (*o*-PA), isophthaloyl dichloride (*m*-PA), terephthaloyl dichloride (*p*-PA)), benzoyl chloride (BzCl) were carried out in the presence of triethylamine (Et_3N) to obtain optically active polyesters. The results are summarized in Table 1.

Table 1. Polycondensation of DHRSI and *x*-PA in THF at -40 °C

run	DHRSI[a] (mol/L)	*x*-PA[b]	Time (h)	Yieid[c] (%)	*Mn* [d] x 10^{-2}	*Mw/Mn*[d]	$[\alpha]_D$[e] (deg.)
1	DHBnSI	*o*-PA	96	46	4.7	1.86	+94.9
2	(0.23)	*m*-PA	96	92	11.2	2.11	+89.4
3		*p*-PA	144	43	9.5	3.75	+198.1
4	DHCHSI	*o*-PA	120	23	4.7	1.97	+66.5
5	(0.23)	*m*-PA	96	69	9.8	2.39	+156.8
6		*p*-PA	98	35	10.0	3.18	+206.1
7	DHPhSI	*o*-PA	122	53	5.8	1.79	-11.0
8	(0.08)	*m*-PA	96	20	2.4	1.40	+27.8
9		*p*-PA	99	60	1.8	1.28	+0.9
10	DHBnSI	BzCl	96	63	-	-	+141.4
11	DHCHSI	BzCl	20	21	-	-	+88.7
12	DHPhSI	BzCl	11	84	-	-	+108.3

[a] DHRSI=0.5 g. [b] *o*-PA; Phthaloyl dichloride, *m*-PA; Isophthaloyl dichloride, *p*-PA; Terephthaloyl dichloride, BzCl; Benzoyl chloride, [DHRSI] / [*x*-PA]=1.0. [c] *n*-Hexane-MeOH insoluble part. [d] By GPC. [e] *c* = 1.0g/dl, *l* = 5cm, in THF.

The polymers had low number-average molecular weights (*Mn*) of 180 ~ 1120 by gel permeation chromatography (GPC) analyses based on standard polystyrene and *Mw/Mn* values were 1.28 ~ 3.75. No polymers were obtained by the polycondensation at 0 °C owing to side reactions. Poly(DHBnSI/*x*-PA), poly(DHCHSI/*x*-PA) and model compounds (DBzRSI; runs 10 - 12) obtained with Et_3N (10 mol%) as base showed *dextro* specific rotations. Poly(DHCHSI/*p*-PA) prepared with Et_3N at -40 °C for 98 h showed the highest specific rotation ($[\alpha]_D$ = +206.1°). But the absolute values of specific rotation of polymer obtained from DHPhSI and *x*-PA decreased (runs 7 - 9). In particular poly(DHPhSI/*o*-PA) exhibited *levo* specific rotation ($[\alpha]_D$ = -11.0°). Figure 1 depicts GPC curves of poly(DHRSI/*x*-PA) monitored with UV and polarimetric detectors.

The GPC curves of poly(DHBnSI/*x*-PA) and poly(DHCHSI/*x*-PA) obtained by polarimetric detection almost corresponded to those by UV detector. The results suggest that chiroptical properties of the polymers exist in the main chain homogeneously. But the GPC curve of poly(DHPhSI/*o*-PA) by polarimetric detector (α_{Hg}) showed *dextro* specific rotation at a low molecular weight fraction and *levo* specific rotation at a high molecular weight fraction.

The polyesters prepared from DHRSIs had *dextro* specific rotation values except for poly(DHPhSI/*o*-PA). The authors synthesized DBzRSI as model compounds for poly(DHRSI/*x*-PA). DBzRSIs were prepared from DHRSI and benzoyl chloride in the presence of Et_3N at -40 °C. Each model compound containing (*R*)-configuration had *dextro* specific rotation (+88.7 ~ +141.4°).

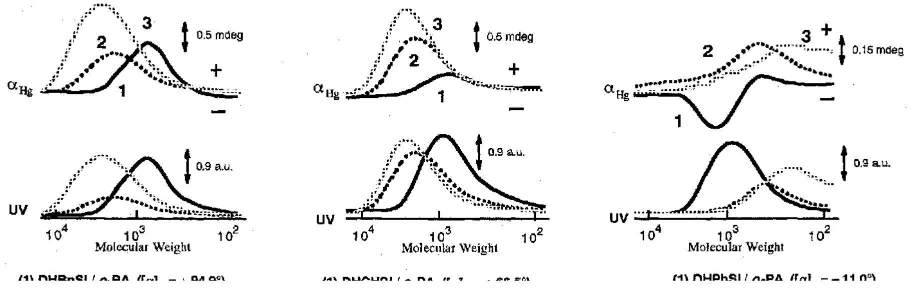


Figure 2 shows relationship between specific rotation of poly(DHRSI/*o*-PA) prepared by runs 1 and 7 in Table 1 and temperature. Specific rotation of poly(DHBnSI/*o*-PA) decreased with temperature. The temperature coefficient ($\Delta[\alpha]_D/\Delta T$) was 0.14. On the other hand, specific rotations of poly(DHPhSI/*o*-PA) shifted from negative to positive values with increasing temperature. Poly(DHPhSI/*o*-PA) exhibited *dextro* specific rotation ($[\alpha]_D$ = +2.8°) at 48 °C. In spite of low specific rotation (-11.0° at 25 °C), the absolute values of $\Delta[\alpha]_D/\Delta T$ (0.53) of poly(DHPhSI/*o*-PA) were larger than that (0.14) of poly(DHBnSI/*o*-PA).

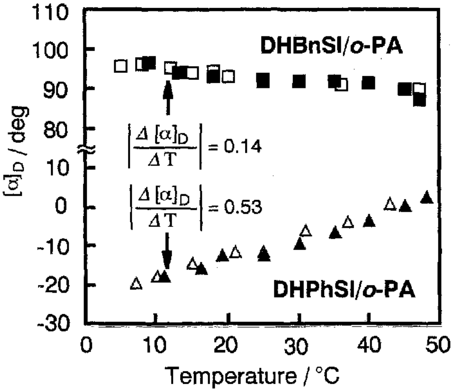


Figure 2. Effects of measurement temperature on specific rotation ($[\alpha]_D$) of DHRSI/*o*-PA in THF: (■, ▲) heating; (□, △) cooling.

Typical CD and UV spectra of poly(DHPhSI/*x*-PA) and DBzPhSI (Table 1, runs 7, 8, 9 and 12) are shown in Figure 3. The UV spectrum of DBzPhSI showed the electric transition dipoles (^1L_a) of benzoate at about 230 nm (Figure 3). The ^1L_a transition is polarized along the axis of benzoate chromophore, which is perpendicular to the main chain of poly(DHPhSI/*x*-PA). The CD spectrum of DBzPhSI exhibited a positive first Cotton effect at 244 nm ($[\theta]_{244}$ = *ca.* +99000 deg•cm^2•dmol^{-1}) and a negative second one at 228 nm ($[\theta]_{228}$ = *ca.* -46000 deg•cm^2•dmol^{-1}) (Figure 3). According to the exciton chirality method [7, 8], the CD curve of DBzPhSI (curve 4 in Figure 3) had positive chirality in which two benzoate groups were twisted clockwise, *i.e.*, (*R*,*R*)-configuration. On the other hand, the CD curves of poly(DHPhSI/*x*-PA) were similar to that of DBzPhSI. This positive CD pattern shows that the electric transition dipoles (^1L_a) of the phthalate chromophore constitute positive chirality. Judging from the result of positive chirality, vicinal phthalate groups of the poly(DHPhSI/*x*-PA) are situated in positions of twisted clockwise and non-strain conformation.

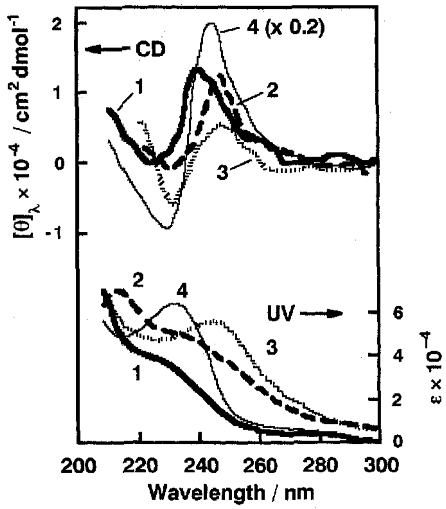


Figure 3. CD and UV spectra for poly(DHPhSI/*x*-PA) and DBzPhSI at (1) poly(DHPhSI/*o*-PA) (Table 1, run 7), (2) poly(DHPhSI/*m*-PA) (run 8), (3) poly(DHPhSI/*p*-PA) (run 8), and (4) DBzPhSI (run 12).

Chiroptical properties of poly(DHPhSI/*x*-PA) could be attributed to higher order structure such as helical structure (Figure 4), judging from GPC curves, CD spectra and effects of measurement temperature on specific rotation. The imide ring and the *N*-substituted phenyl group lie on the same plane because of their conjugated structures. In addition, polymers contained a rigid imide ring and phenyl group at the main chains. That is, the conformational flexibility of poly(DHPhSI/*x*-PA) is low. When the structure of polymer forms a 3_1 helix, highly ordered structures of poly(DHPhSI/*x*-PA)s were more stable than that of poly(DHCHSI/*x*-PA)s or poly(DHBnSI/*x*-PA)s by π–π stacking interactions.

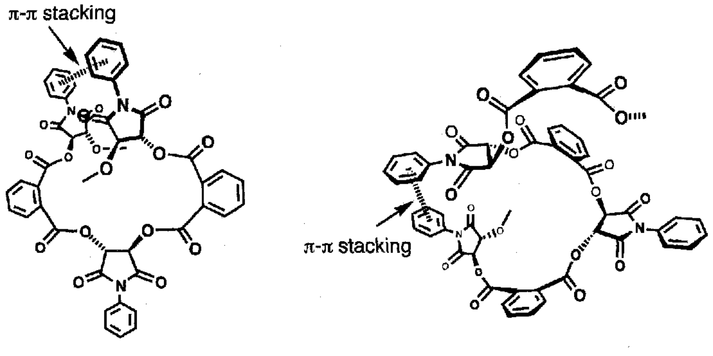


Figure 4. Helical structure of poly(DHPhSI/*o*-PA).

Conclusions

(1) Polycondensations of (*3R, 4R*)-3,4-dihydro-*N*-substituted succinimide (DHRSI) and phthaloyl dichloride (*x*-PA) were carried out in the presence of triethylamine (Et_3N) to obtain optically active polyesters ($[\alpha]_D$ = -11.0° to +206.1°).

(2) Poly(DHCHSI/*p*-PA) prepared with Et_3N at -40 °C for 98 h showed the highest specific rotation ($[\alpha]_D$ = +206.1°).

(3) The GPC curve of poly(DHPhSI/*o*-PA) by polarimetric detector (α_{Hg}) showed *dextro* rotation at a low molecular weight fraction and *levo* rotation at a high molecular weight fraction.

(4) The *levo* specific rotation of poly(DHPhSI/*o*-PA) may be considered to result from "conformational chirality".

Acknowledgements

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