Synthesis and Structure of Poly(*N*-propargylbenzamides) Bearing Chiral Ester Groups

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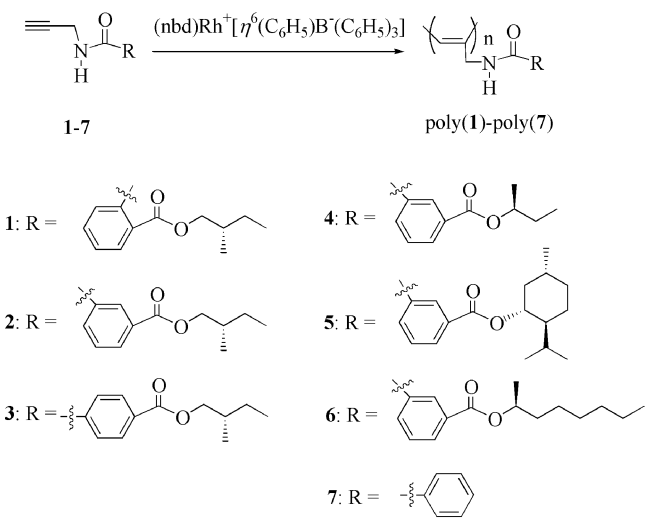
ABSTRACT: *N*-Propargylbenzamides having chiral ester groups on the benzene ring, **1**−**6**, were polymerized with (nbd)$Rh^+[\eta^6$-$C_6H_5B^-(C_6H_5)_3]$ to afford soluble polymers with moderate molecular weights (M_n = 34 000−100 000) in good yield. The ^{1}H NMR spectra demonstrated that the polymers have stereoregular structures (cis = 91−100%). The influence of the substitution position for the chiral ester group on the secondary structure was examined. From the comparison of the CD effects of poly(**1**)−poly(**3**), the meta-substituted polymer was proven to possess a one-handed helical conformation. When the chiral center was closer to the benzene ring or chiral ester group was bulkier, the polymers showed more intense chiroptical properties. A variable temperature CD spectroscopic study showed that the helical structure of poly(**2**) and poly(**6**) was thermally stable. However, the CD spectra of poly(**4**) and poly(**5**) were inverted in sign on temperature change in chloroform or toluene, meaning that the helix inversion took place. The temperature of helix inversion could be controlled by copolymerizing with *N*-propargylbenzamide (**7**).

Introduction

One of the representative secondary conformations of polymer is the helical structure. Much attention has been paid to helical polymers owing to their unique functions such as molecular recognition ability and catalytic ability for asymmetric synthesis.[1] Previous intensive efforts have made it possible to produce a variety of well-ordered helical polymers. The helical polymers are classified into two types. One is the polymers with stable helical conformation,[2] in which the helix−helix or helix−coil transition does not occur at all due to their rigid main chain. The other is the polymers having dynamic helix,[3] which have a stiff but not rigid main chain. These polymers undergo helix−helix and/or helix-random coil interconversion due to the small energetic barriers for helix reversal. The polymeric materials that can change the helix sense by external stimuli are attracting much attention owing to the potential application in devices such as molecular switches, data storage, and transmission.[4]

Recently, we showed that stereoregular poly(*N*-propargylalkylamides) adopt a helical structure which is stabilized by the intramolecular hydrogen bonds between the pendant amide groups.[5] Poly(*N*-propargylalkylamides) undergo a helix−random coil transition upon sensing external stimuli such as changes in temperature and solvent because the intramolecular hydrogen bonds can be readily broken by external stimuli.[6,7] The polymers also show thermochromism and solvatochromism upon this conformational change.[6] On the contrary, the secondary conformation of poly(*N*-propargylarylamides) has not been investigated in detail because of their poor solubility.[7] In the present study, we synthesized poly(*N*-propargylbenzamides) having chiral ester groups, poly(**1**)−poly(**6**) (Scheme 1). It has been found that the position and structure of the chiral ester group significantly influence the secondary structure. We further show that poly(**4**) and poly(**5**) undergo the thermally driven inversion of the screw sense.

Scheme 1



Experimental Section

Materials. The solvents were distilled by usual methods prior to use. Propargylamine (Aldrich), (*S*)-(−)-2-methyl-1-butanol (Tokyo Kasei), (*S*)-(−)-2-butanol (Aldrich), (*S*)-(−)-2-octanol (Azmax), phthaloyl chloride (Wako), isophthaloyl chloride (Wako), terephthaloyl chloride (Tokyo Kasei), pyridine (Wako), isobutyl chloroformate (Wako), and 4-methylmorpholine (Wako) were used without further purification. (nbd)Rh^+-[η^6-$C_6H_5B^-(C_6H_5)_3$] was prepared as reported.[8a]

Monomer Synthesis. Synthesis of **1** is described as a typical procedure. A mixture of (*S*)-(−)-2-methyl-1-butanol (5.4 mL, 49.3 mmol) and pyridine (8.7 mL, 98.7 mmol) was slowly added to a THF solution (150 mL) of phthaloyl chloride (10 g, 49.3 mmol) at 0 °C. After the reaction mixture was refluxed for 6 h, water (20 mL) was added, and the mixture was further refluxed for 6 h. The mixture was washed with 2 M aqueous HCl and then water and concentrated to give (*S*)-2-(2-methylbutoxycarbonyl)benzoic acid in 68% yield. Isobutyl chloro-

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formate (4.60 mL, 33.8 mmol) was added to a THF solution (100 mL) of the resulting (*S*)-2-(2-methylbutoxycarbonyl)-benzoic acid (7.97 g, 33.8 mmol) and 4-methylmorpholine (3.41 mL, 33.8 mmol) at 0 °C. After 15 min, propargylamine (2.33 mL, 33.8 mmol) was added to the solution. The solution was stirred at room temperature for 1 h. After the white precipitate was filtered off, the filtrate was concentrated. Ethyl acetate (ca. 100 mL) was added to the residue, and the solution was washed with 2 M aqueous HCl and saturated aqueous $NaHCO_3$, dried over $MgSO_4$, and concentrated. Monomer **1** was isolated (1.62 g, 5.92 mmol, 12%) by flash column chromatography on silica gel (hexane/AcOEt, 3/2, v/v). Monomers **2**−**6** were prepared in a similar way. The spectral data are as follows.

1: yield 12%; mp 49 °C; $[\alpha]_D = +4.18°$. IR (KBr): 3324, 2963, 1713, 1647, 1529, 1261, 1134, 794 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, J = 7.32 Hz), 0.92 (d, 3H, J = 6.84 Hz), 1.19 (m, 1H), 1.43 (m, 1H), 1.76 (m, 1H), 2.22 (d, 1H, J = 2.44 Hz), 4.11 (d, 2H, J = 4.39 Hz), 4.02 (d, 2H, J = 6.81 Hz), 4.16 (d, 2H, J = 2.44 Hz), 6.32 (s, 1H), 7.40−7.48 (m, 4H), 7.81 (d, 1H, J = 6.35 Hz). ^{13}C NMR ($CDCl_3$): δ 11.13, 16.34, 25.92, 33.99, 70.27, 71.81, 71.88, 79.16, 127.64, 129.38, 129.71, 129.94, 130.00, 131.75, 166.63, 168.79. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.33; H, 6.96; N, 5.13. Found: C, 70.28; H, 6.72; N, 5.31.

2: yield 35%; mp 34 °C; $[\alpha]_D = +4.61°$. IR (KBr): 3333, 2968, 1713, 1649, 1541, 1263, 991, 738 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = Hz), 0.87 (d, 3H, J = 6.83 Hz), 1.13 (m, 1H), 1.37 (m, 1H), 1.72 (m, 1H), 2.16 (d, 1H, J = Hz), 4.02 (d, 2H, J = 4.40 Hz), 4.14 (d, 2H, J = 2.44 Hz), 6.70 (s, 1H), 7.38 (1H, J = Hz), 7.86 (1H, J = Hz), 7.92, (1H, J = Hz), 8.25 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 11.18, 16.41, 26.01, 34.15, 69.96, 71.84, 71.92, 79.23, 127.73, 128.77, 130.79, 131.74, 132.50, 134.00, 165.86, 166.21. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.33; H, 6.96; N, 5.13. Found: C, 70.13; H, 7.04; N, 4.92.

3: yield 18%; mp 102 °C; $[\alpha]_D = +5.24°$. IR (KBr): 3308, 2964, 1724, 1641, 1541, 1275, 1018, 729 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.86 (t, 3H, J = 8.79 Hz), 1.00 (d, 3H, J = 6.84 Hz), 1.27 (m, 1H), 1.49 (m, 1H), 1.85 (m, 1H), 2.27 (d, 1H, J = 2.44 Hz), 4.19 (d, 2H, J = 5.85 Hz), 4.24 (d, 2H, J = 2.44 Hz), 6.74 (s, 1H), 7.85 (d, 2H, J = 8.30 Hz), 8.70 (d, 2H, J = 8.30 Hz). ^{13}C NMR ($CDCl_3$): δ 11.21, 16.43, 26.07, 34.21, 69.92, 71.88, 72.06, 79.16, 127.04, 127.13, 129.69, 129.78, 133.27, 137.44, 165.79, 166.30. Anal. Calcd for $C_{16}H_{19}NO_3$: C, 70.33; H, 6.96; N, 5.13. Found: C, 70.17; H, 6.98; N, 5.15.

4: yield 15%; mp 75 °C; $[\alpha]_D = +25.7°$. IR (KBr): 3277, 2974, 1718, 1638, 1541, 1265, 733 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.87 (t, 3H, J = 7.19 Hz), 1.24 (d, 3H, J = 6.39 Hz), 1.62 (m, 2H), 2.20 (d, 1H, J = 2.44 Hz), 4.18 (d, 2H, J = 2.44 Hz), 6.42 (s, 1H), 7.43 (t, 1H, J = 7.59 Hz), 7.93 (d, 1H, J = 7.59 Hz), 8.08 (d, 1H, J = 7.59 Hz), 8.29 (s, 1H). ^{13}C NMR: δ 10.56, 20.75, 29.44, 30.09, 72.43, 73.83, 79.43, 128.50, 129.72, 131.68, 132.24, 133.45, 134.58, 166.36, 155.73. Anal. Calcd for $C_{15}H_{17}NO_3$: C, 69.50; H, 6.56; N, 4.75. Found: C, 69.56; H, 5.35; N, 6.64.

5: yield 35%; mp 38 °C; $[\alpha]_D = -82.5°$. IR (KBr): 3290, 2957, 1716, 1649, 1458, 1259, 731 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.74 (d, 3H, J = 6.84 Hz), 0.87 (t, 6H, J = 6.84 Hz), 1.07 (q, 2H, J = 11.72 Hz), 1.21 (d, 1H, J = 7.33 Hz), 1.50 (t, 2H, J = 11.71 Hz), 1.68 (m, 2H), 1.88 (m, 1H), 2.00 (m, 1H), 2.25 (d, H, J = 2.42 Hz), 4.23 (d, 2H, J = 2.44 Hz), 4.91 (dt, 1H, J = 4.39, 10.75 Hz), 6.47 (s, 1H), 7.49 (t, 1H, J = 7.81 Hz), 7.98 (d, 1H, J = 7.81 Hz), 8.13 (d, 1H, J = 7.81 Hz), 8.35 (s, 1H). ^{13}C NMR: δ 16.35, 20.71, 23.45, 26.45, 29.86, 31.44, 34.19, 40.82, 47.13, 71.98, 72.17, 79.213, 127.62, 128.83, 131.24, 131.86, 132.63, 133.97, 165.32, 166.17. Anal. Calcd for $C_{21}H_{27}NO_3$: C, 73.90; H, 7.92; N, 4.11. Found: C, 73.72; H, 7.85; N, 3.95.

6: yield 32%; mp 25 °C; $[\alpha]_D = +30.3°$. IR (KBr): 3361, 2932, 2127, 1716, 1651, 1537, 1261, 785 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.82 (t, 3H, J = 6.40 Hz), 1.13 (m, 11H), 1.56 (m, 1H), 1.70 (m, 1H), 2.32 (s, 1H), 4.24 (d, 2H, J = 2.44 Hz), 5.13 (q, 1H, J = 6.01 Hz), 6.84 (s, 1H), 7.49 (t, 1H, J = 7.81 Hz), 8.01 (d, 1H, J = 7.81 Hz), 8.14 (d, 1H, J = 7.81 Hz), 8.63 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 13.96, 19.94, 20.93, 22.48, 25.32, 29.03, 31.61, 35.89, 71.75, 72.28, 79.25, 127.68, 128.66, 131.19, 131.60, 132.58, 133.93, 165.35, 166.23. Anal. Calcd for $C_{19}H_{25}NO_3$: C, 72.38; H, 7.94; N, 4.44. Found: C, 72.66; H, 7.91; N, 4.38.

Polymerization Procedures. A $CHCl_3$ solution of the monomers ($[M]_{total}$ = 2 M) was added to a $CHCl_3$ solution of (nbd)$Rh^+[\eta^6$-C_6H_5B−$(C_6H_5)_3]$ ([monomer]/[cat] = 100) under dry nitrogen, and the solution was kept at 30 °C for 1 h. The solution was poured into a large amount of methanol to precipitate the polymers. The resulting polymers were collected by filtation and dried under reduced pressure.

Poly(**1**): IR ($CHCl_3$): 3308, 3020, 1717, 1647, 1538, 1219, 1084, 779 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.78−0.99 (6H, CH(CH_3)-CH_2CH_3), 0.99−1.18 (1H, CH_2CH_3), 1.18−1.43 (1H, CH_2CH_3), 1.43−1.76 (1H, $CH(CH_3)CH_2$), 3.60−4.41 (4H, CH═CCH_2, (C═O)OCH_2), 5.90−6.39 (1H, CH═CCH_2), 7.02−7.75 (5H, NH, Ar).

Poly(**2**): IR ($CHCl_3$): 3335, 3027, 1719, 1632, 1545, 1219, 791 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.76−1.01 (6H, CH(CH_3)-CH_2CH_3), 1.01−1.22 (1H, CH_2CH_3), 1.22−1.43 (1H, CH_2CH_3), 1.43−1.78 (1H, $CH(CH_3)CH_2$), 3.78−4.51 (4H, CH═CCH_2, (C═O)OCH_2), 6.12−6.40 (1H, CH═CCH_2), 7.10−7.48 (1H, Ar), 7.86−8.19 (1H, Ar), 8.19−8.44 (1H, Ar), 8.44−8.75 (1H, Ar), 8.75−9.24 (1H, NH).

Poly(**3**): IR ($CHCl_3$): 3312, 3020, 1717, 1638, 1541, 1211, 754 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.75−1.10 (6H, CH(CH_3)-CH_2CH_3), 1.10−1.36 (1H, CH_2CH_3), 1.36−1.58 (1H, CH_2CH_3), 1.58−1.96 (1H, $CH(CH_3)CH_2$), 3.71−4.31 (4H, CH═CCH_2, (C═O)OCH_2), 5.80−6.28 (1H, CH═CCH_2), 7.22−7.95 (4H, Ar), 7.95−8.38 (1H, NH).

Poly(**4**): IR ($CHCl_3$): 3335, 3020, 1716, 1632, 1543, 1219, 777 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.64−0.99 (3H, CH(CH_3)-CH_2CH_3), 0.99−1.35 (3H, CH(CH_3)CH_2CH_3), 1.35−1.77 (2H, CH(CH_3)CH_2CH_3), 3.80−4.71 (2H, CH═CCH_2), 4.71−5.18 (1H, CH(CH_3)CH_2CH_3), 5.90−6.49 (1H, CH═CCH_2), 7.28−7.51 (1H, Ar), 7.81−8.19 (1H, Ar), 8.19−8.42 (1H, Ar), 8.42−8.77 (1H, Ar), 8.77−9.31 (1H, NH).

Poly(**5**): IR ($CHCl_3$): 3343, 3020, 1711, 1635, 1541, 1219, 779 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.76−1.01 (6H, CH(CH_3)-CH_2CH_3), 1.01−1.22 (1H, CH_2CH_3), 1.22−1.43 (1H, CH_2CH_3), 1.43−1.78 (1H, $CH(CH_3)CH_2$), 3.78−4.51 (4H, CH═CCH_2, (C═O)OCH_2), 6.12−6.40 (1H, CH═CCH_2), 7.10−7.48 (1H, Ar), 7.86−8.19 (1H, Ar), 8.19−8.44 (1H, Ar), 8.44−8.75 (1H, Ar), 8.75−9.24 (1H, NH).

Poly(**6**): IR ($CHCl_3$): 3346, 3019, 1715, 1634, 1539, 1217, 787 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.68−0.95 (3H, CH_2CH_3), 0.95−1.38 (11H, CH(CH_3)$CH_2CH_2CH_2CH_2CH_2CH_3$), 1.38−1.52 (1H, CH(CH_3)$CH_2CH_2CH_2CH_2CH_2CH_3$), 1.52−1.78 (1H, CH-(CH_3)$CH_2CH_2CH_2CH_2CH_2CH_3$), 3.81−4.62 (2H, CH═CCH_2), 4.82−5.18 (1H, $CH(CH_3)CH_2$), 5.98−6.40 (1H, CH═CCH_2), 7.30−7.58 (1H, Ar), 7.96−8.19 (1H, Ar), 8.19−8.42 (1H, Ar), 8.42−8.76 (1H, Ar), 8.76−9.18 (1H, NH).

Measurements. Molecular weights and molecular weight distributions of polymers were estimated by GPC (Shodex KF-850L columns) calibrated by using standard polystyrenes in chloroform solution. NMR spectra were recorded on a JEOL EX-400 spectrometer. IR spectra were obtained with a Shimadzu FTIR-8100 spectrophotometer. UV−vis spectra were recorded on a JASCO V-500 spectrophotometer. Optical rotation was measured with a JASCO 600 spectropolarimeter. CD spectra were recorded on a JASCO V-530 spectropolarimeter.

Results and Discussion

Polymer Synthesis. Polymerization was performed using a rhodium catalyst, (nbd)$Rh^+[(C_6H_5)B$−$(C_6H_5)_3]$, which is effective for the polymerization of *N*-propargylamides to afford stereoregular, cis−transoidal polymers.[5,6] The polymerization results of **1**−**6** which have chiral ester groups on the phenyl ring are summarized in Table 1. Polymers with moderate molecular weights (M_n = 34 000−100 000) were obtained in good yield. Poly(*N*-propargylbenzamide), poly(**7**), did not dissolve in common organic solvents such as toluene, $CHCl_3$ and THF. On the other hand, other polymers, poly(**1**)−poly(**6**), were soluble in organic solvents.

The stereoregularity of the polymers was examined by ^1H NMR spectroscopy. Poly(**1**)−poly(**6**) exhibited a well-resolved signal at around 5.8 ppm, which can be

Table 1. Polymerization of 1−6

monomer		yield			cis	
	$[\alpha]_D$ (deg)	(%)[a]	M_n[b]	M_w/M_n[b]	(%)[c]	$[\alpha]_D$ (deg)[d]
1	(+4.18)	67	34 000	4.78	100	−29.4
2	(+4.61)	57	100 000	4.67	100	+365.0
3	(+5.24)	63	38 000	6.74	91	−51.1
4	(+25.7)	63	51 000	4.04	100	+573.0
5	(−82.5)	70	98 000	6.99	100	+380.0
6	(+30.3)	60	51 000	5.19	95	+586.0

[a] Methanol-insoluble part. [b] Estimated by GPC ($CHCl_3$, PSt standards). [c] Determined by ^1H NMR. [d] $c = 0.0880-0.108$ g/dL in $CHCl_3$.

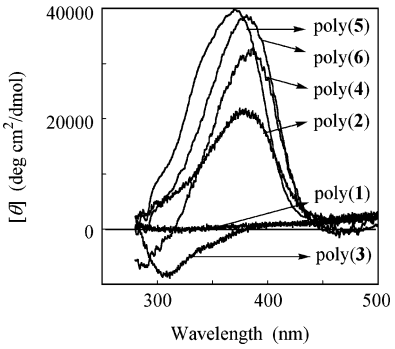


Figure 1. CD spectra of poly(**1**)−poly(**6**) in $CHCl_3$ at room temperature.

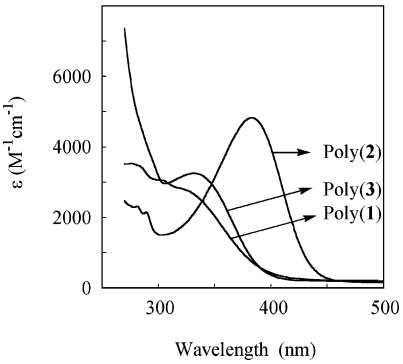


Figure 2. UV spectra of poly(**1**)−poly(**3**) in $CHCl_3$ at room temperature.

assigned to the olefinic protons of the cis−transoidal main chain. The cis contents were estimated to be 91−100% by the integrated intensities of the ^1H NMR signals. The peaks of the protons close to the main chain are very broad for poly(*N*-propargylalkylamides) due to the limited main-chain mobility.[5] On the other hand, these poly(*N*-propargylbenzamides) displayed clear signals, indicating their main-chain flexibility.

Secondary Conformation. The CD and UV−vis spectra of poly(**1**)−poly(**6**) are shown in Figures 1 and 2, respectively. To find the optimal structure to induce the helical structure, the CD spectra of poly(**1**)−poly(**3**), which have the same chiral ester group at different substitution positions, were compared. Poly(**2**) showed a large $[\alpha]_D$ (Table 1) and intense CD effect in the region of the main-chain absorption in $CHCl_3$ at room temperature. On the other hand, poly(**1**) did not show a clear CD, and poly(**3**) displayed only a weak CD (Figure 1). We have reported that the absorptions of poly(*N*-propargylalkylamides) at around 320 and 390 nm correspond to the disordered and helical conformations, respectively.[6] Poly(**2**) showed the absorption centered at 380 nm, while poly(**1**) and poly(**3**) displayed absorption maxima at 320 nm (Figure 2). These results lead to a conclusion that the main chain of poly(**2**) exists in a helical conformation with an excess of one-handed screw sense while poly(**1**) and poly(**3**) take a random conformation. Therefore, introduction of a chiral ester group at the meta position of the phenyl ring is suitable to induce the helical structure.

Table 2. IR Spectral Data of Poly(1)−Poly(6) in $CHCl_3$[a]

polymer	amide I (cm^{-1})	amide II (cm^{-1})
poly(**1**)	1647	1537
poly(**2**)	1632	1545
poly(**3**)	1637	1541
poly(**4**)	1632	1543
poly(**5**)	1635	1541
poly(**6**)	1634	1539

[a] $c = 48$ mM.

Next, the CD spectra of poly(**2**), poly(**4**), and poly(**5**) which have various chiral ester groups at the meta position were compared. These polymers showed very intense CD effects and large $[\alpha]_D$ in $CHCl_3$ at room temperature, indicating that they have helical conformation with a biased screw sense in solution. The magnitude of the Cotton effects of poly(**5**) and poly(**6**) was larger than that of poly(**2**). Thus, when the asymmetric carbon is located closely to the main chain or when the pendant group is bulky, the screw sense is more effectively biased.

To investigate the nature of the hydrogen bonding of the amide groups, IR spectra of poly(**1**)−poly(**6**) were measured in $CHCl_3$ (Table 2). Because the amide I band of poly(**1**) (1647 cm^{-1}) stayed at the high-frequency region compared to other polymers, its amide group was not effectively hydrogen-bonded. However, the amide II band of poly(**1**) (1537 cm^{-1}) was located in the hydrogen-bonded region. These results indicate that the carbonyl moiety of the ester group and N−H moiety of the amide group form the cyclic hydrogen bond and that this cyclic hydrogen bond hinders the intramolecular hydrogen bond between the pendant amide groups.[9] Thus, poly(**1**) cannot form the helical structure. Because the amide I band of poly(**3**) (1637 cm^{-1}) was observed at almost the same position as the other polymers, the absence of the helical conformation in poly(**3**) is not due to the lack of the intramolecular hydrogen bond. Probably, the rigidity of polymer backbone is not enough to take the helical conformation.

Thermally Driven Helix-Sense Inversion. To examine the thermal stability of the helical conformation, we measured CD spectra of poly(**2**), poly(**4**), poly(**5**), and poly(**6**) in $CHCl_3$ or toluene at various temperatures. The CD spectra of the polymers with long alkyl chain on the phenyl ring such as poly(**2**) and poly(**6**) showed increased molar ellipticity by lowering temperature. However, the shape did not change (Figure 3). On the other hand, the shape of the CD effects of poly(**4**) and poly(**5**) remarkably changed with changing temperature (Figure 4). When the temperature was lowered, for example, the Cotton effects of poly(**4**) decreased in intensity, and the sign of the Cotton effect was inverted reversibly at around −5 °C (Figure 4a). The CD spectra at 55 °C was almost mirror-imaged to that at −40 °C except for a slight shift of the absorption. This means that the helix-sense inversion occurs by lowering temperature. Because the screw sense of poly(**4**) at 55 and −40 °C was opposite to each other, these two helical conformations are diastereomers. This is the reason for the shift of the CD absorption wavelength of poly(**4**) upon the change in temperature. On the other

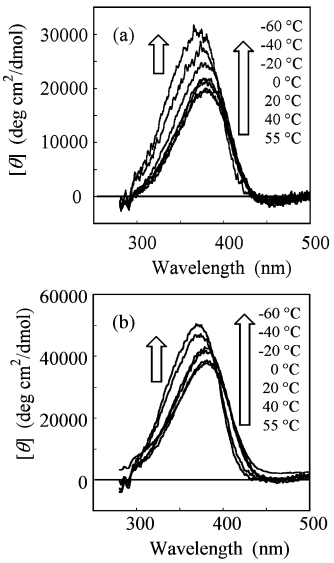


Figure 3. Variable temperature CD spectra of (a) poly(**2**) and (b) poly(**6**) in $CHCl_3$.

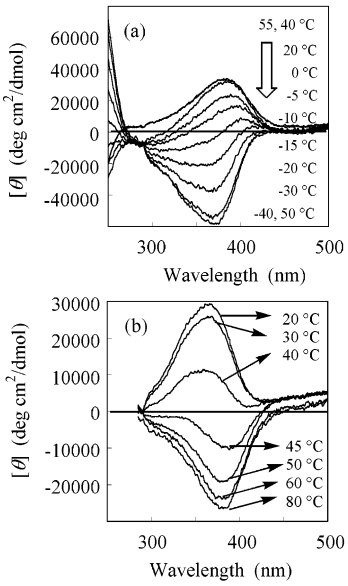


Figure 4. Variable temperature CD spectra of (a) poly(**4**) in $CHCl_3$ and (b) poly(**5**) in toluene.

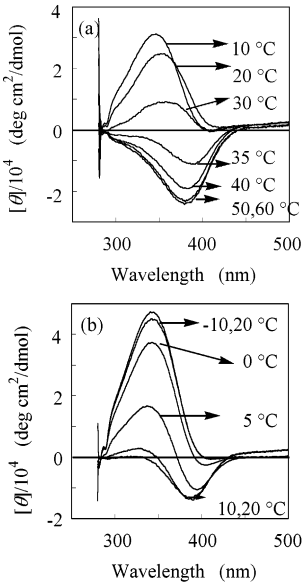


Figure 5. Variable temperature CD spectra of poly(**5**-*co*-**7**) (a) (**5**/**7** = 95/5) (b) (**5**/**7** = 78/22) in toluene.

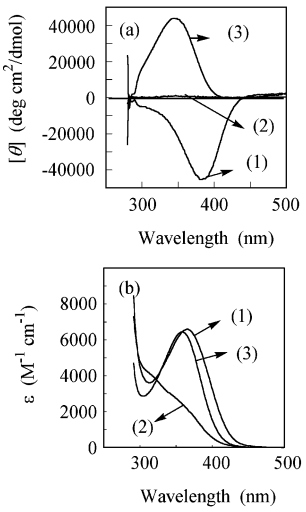
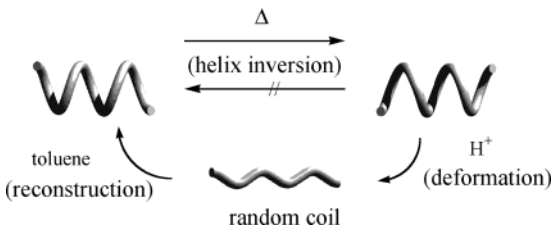


Figure 6. (a) CD and (b) UV spectra of poly(**5**) in toluene. (1) Just after the thermally induced helix inversion, (2) after the TFA treatment, and (3) after the reconstruction of the original helical conformation.

hand, the helix-sense inversion of poly(**5**) inverted upon heating. As shown in Figure 4, the CD spectra of poly(**5**) decreased in intensity upon heating, and the helix-sense transition occurred at 43 °C. Such a helix−helix transition occurs as a result of the changes in enthalpy and entropy terms in Gibbs free energy equation being the same sign. Thus, the free energy difference between the right- and left-handed conformations changes in sign as a function of temperature.[10] Julian et al. reported that a polysilane having chiral pendant groups undergoes a thermally induced helix−helix transition. Furthermore, they have shown that the helix−helix transition temperature can be controlled by the copolymerization with an achiral comonomer.[11] Such control of the helix-sense transition was also possible by the copolymerization of **5** with an achiral monomer **7**. For example, the transition temperatures of the homo- and copolymers with a ratio of **5**:**7** = 100:0, 95:5, and 78:22 were 43, 32, and 5 °C, respectively (cf. Figure 5).[12] When the ratio of **7** was increased by 5%, the transition temperature decreased by about 10 °C. From these results, we can conclude that when the bulkiness of side group is reduced, the transition temperature decreases. In other words, the helix−helix transition temperature can be adjusted by the composition ratio of the copolymer.

It is very interesting that, in contrast to poly(**4**), the helix transition of poly(**5**) was irreversible. For example, when a toluene solution of poly(**5**) was heated at 70 °C for 30 min, the initially positive Cotton effect changed to a negative one (Figure 6a-1). However, this negatively signed CD signal did not revert to the positively signed one even when the solution was cooled to 20 °C. Only a few percent of the original spectrum was restored when the solution was kept 20 °C for 24 h. A similar behavior was also observed for poly(**5**-*co*-**7**) (**5**/**7** = 95/5). Because poly(**5**) may be applied as a data storage material, we tried to restore the original helix-sense conformation of helix-inverted polymer according to the cycle described in Scheme 2. In an attempt to deform helical conformation of helix-inverted poly(**5**), the polymer solution was poured into methanol, which can destroy the helical conformation of poly(*N*-propargylalkylamides). How-

Scheme 2



ever, the CD and UV spectrum of the resulting polymer in toluene was almost the same as the spectrum of helix-inverted polymer (Figure 6-1). This means that the treatment with methanol could not destroy the helical structure. This is in contrast to the previous results about poly(*N*-propargylalkylamides); e.g., the helical conformation of poly(*N*-propargyl-3-methylbutanamide) is readily deformed by treating with methanol. Deformation of poly(**5**) was achieved by adding a few drops of trifluoroacetic acid (TFA). The CD and UV spectrum of this TFA-treated sample are shown in Figure 6-2. The CD effect disappeared, and the absorption shifted to 320 nm, which indicates that the helical conformation was completely deformed. When the TFA-treated sample was purified by reprecipitation and dissolved in toluene again (Figure 6-3), it showed the CD effect identical in shape and intensity to the original one. This means that the original conformation is recovered by this acid-catalyzed deformation process (Scheme 2).[13]

Conclusion. Poly(*N*-propargylbenzamides) having chiral ester groups at the meta position have proven to exist in the helical conformation. When the chiral center is located near the benzene ring or when the chiral ester group is bulky, the screw sense of helix is more effectively biased. Some of poly(*N*-propargylphenylamides) such as poly(**4**) and poly(**5**) undergo helix-sense inversion driven by the change in temperature. The helix-sense inversion of poly(**4**) was reversible, whereas that of poly(**5**) was irreversible. The helix−helix transition temperature can be adjusted by the composition of copolymer of **5** with **7**. The original helix-sense could be restored when the helix with inverted screw sense was deformed by acid and then dissolved in acid-free solvent. This characteristic would allow poly(*N*-propalgylbenzamides) to be applied as a new data storage material.

References and Notes

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(12) The molecular weights of poly(**5**-*co*-**7**) (**5**/**7** = 90/10 and 80/20 in feed) were 60 000 (M_w/M_n = 2.96) and 45 000 (M_w/M_n = 4.03), respectively.
(13) The molecular weight of poly(**5**) did not change, and isomerization or degradation did not occur during the acid treatment.

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