Articles

Chirality Induction in Cyclocopolymerization. 13. Structural Effect of 1,3-Diol as Chiral Templates in the Cyclocopolymerization of Bis(4-vinylbenzoate)s with Styrene

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ABSTRACT: Two diastereomeric chiral cycloalkanediols such as (1*S*,2*R*)-2-hydroxymethyl-1-cyclohexanol (**a**) and (1*S*,2*S*)-2-hydroxymethyl-1-cyclohexanol (**b**), which were conformational restriction models for (*S*)-1,3-butanediol (**c**), were used as chiral templates to investigate the conformational effect of the 1,3-diol skeleton of the template moiety in the cyclocopolymerization of bis(4-vinylbenzoate)s (**1**) with styrene. The specific rotation for the resulting template-free polymer **3a** was almost twice that for **3b**. In comparison with chiral template **c**, the efficiency of the chirality induction increases in the order of **b** < **c** < **a**. These characteristics of chiral templates were discussed in terms of the conformational distribution of the monomer **1a**−**c**.

Introduction

Asymmetric cyclocopolymerization of a divinyl monomer having a chiral template with an achiral vinyl comonomer is a certain method for producing an optically active polymer.[1] Wulff et al. reported that the asymmetric cyclocopolymerization was essentially based on the chirality imprinting from the template to the polymer main chain using bis(4-vinylphenylborate) with a D-mannitol template.[2] We reported that the optical activity of poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**), which was synthesized by the cyclocopolymerization of bis(4-vinylbenzoate) of a chiral diol template with styrene, was closely connected with the template structure.[3] The chirality induction efficiency depended on the template structures, such as the distance between two 4-vinylbenzoyl groups,[4a] the number of chiral centers,[4b,c] and the steric crowding at the chiral centers in the template.[4d,e] In general, 1,3-diol templates, such as (*S*)-1,3-butanediol and (2*S*,4*S*)-2,4-pentanediol, exhibited higher ability in chirality induction than 1,2- and 1,4-diol templates.

The template ability of (*S*)-1,3-butanediol is lower than that of (2*S*,4*S*)-2,4-pentanediol, which should be caused by the fact that the conformer distribution of (*S*)-1,3-butanediol is broader than that of (2*S*,4*S*)-2,4-pentanediol. Thus, to study the effect of conformer distribution on the chirality induction, it is necessary to manipulate the conformer distribution; e.g., the conformation of acyclic diols can be restricted using an appropriate tether. For (*S*)-1,3-butanediol, the conformation of the skeletal carbons is governed by the connection between the C2 and C4 positions with a

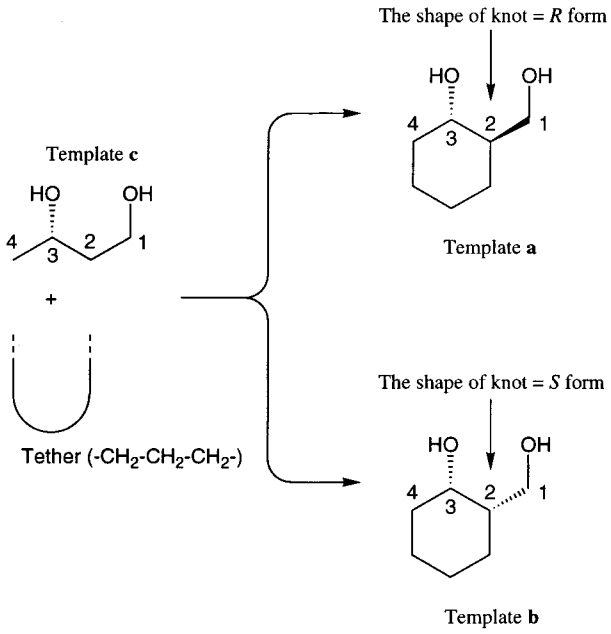

Figure 1. Geometrical restrict for the conformation around C1−C2−C3−C4 by the trimethylene tether. Two shapes of knot are found.

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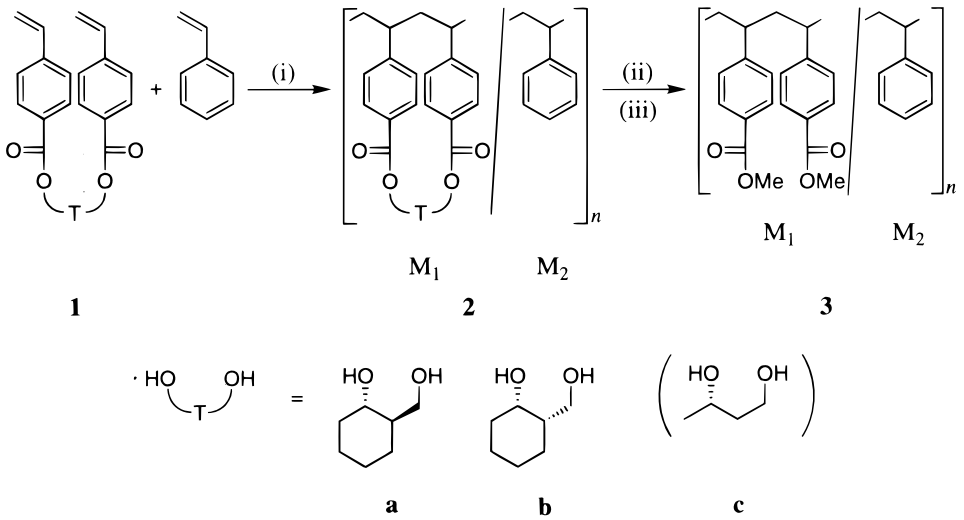
Scheme 1[a]



[a] Conditions: (i) AIBN, toluene, 60 °C; (ii) KOH, MeOH, reflux; (iii) CH_2N_2, Et_2O/benzene.

Table 1. Copolymerizations of 1a and 1b with Styrene To Form Poly[(methyl 4-vinylbenzoate)-*co*-styrene] (3a and 3b)

			polymer **2**[a]				polymer **3**[b]		
monomer	F_1[c]	time, h	yield, %	f_1[d]	M_n (M_w/M_n)[e]	$[\alpha]_{435}$,[f] deg	yield, %	M_n (M_w/M_n)[e]	$[\alpha]_{435}$,[f] deg
1a	0.9	1.2	20	0.98	31 700 (1.97)	+385	52	38 200 (1.56)	−0.6
	0.8	1.3	16	0.94	29 500 (1.98)	+387	68	37 900 (1.55)	−3.8
	0.7	1.3	14	0.88	22 400 (1.78)	+369	77	26 900 (1.54)	−5.1
	0.6	1.5	19	0.84	24 700 (1.59)	+367	43	26 400 (1.52)	−8.8
	0.5	2.0	21	0.76	15 100 (1.77)	+352	41	18 700 (1.43)	−13.8
	0.4	3.0	19	0.65	15 000 (1.62)	+332	69	17 700 (1.41)	−19.9
	0.3	4.0	17	0.57	9 600 (1.73)	+312	64	10 700 (1.51)	−25.6
	0.2	5.5	21	0.45	5 600 (1.82)	+275	68	7 000 (1.57)	−31.1
	0.1	10.5	14	0.30	3 300 (1.77)	+215	41	3 800 (1.65)	−32.4
1b	0.9	1.2	15	0.99	25 000 (1.51)	+270	42	30 200 (2.07)	+0.6
	0.8	2.0	16	0.92	27 000 (1.41)	+277	23	29 200 (1.39)	−1.6
	0.7	2.5	22	0.89	22 000 (1.45)	+283	62	21 100 (1.68)	−3.6
	0.6	3.0	25	0.86	14 000 (1.97)	+274	52	15 000 (1.79)	−5.6
	0.5	2.0	16	0.77	13 000 (1.58)	+262	49	15 700 (1.42)	−8.5
	0.4	3.3	21	0.74	10 000 (1.84)	+250	34	10 000 (1.86)	−10.7
	0.3	6.0	27	0.65	6 300 (1.96)	+233	57	6 500 (2.17)	−14.2
	0.2	5.3	18	0.52	6 400 (1.66)	+217	23	8 300 (1.56)	−15.4
	0.1	15.0	21	0.34	2 800 (1.85)	+169	35	4 300 (1.92)	−18.4

[a] Solvent, toluene; initiator, AIBN; temperature, 60 °C; [**1** + styrene]$_0$ = 0.1 mol L^{-1}; [AIBN]$_0$ = 1 g L^{-1}. [b] Prepared from polymer **2** through hydrolysis using KOH in aqueous MeOH and then treatment with diazomethane. [c] Mole fraction of M_1 in the monomer feed. [d] Mole fraction of M_1 unit in the polymer; determined by ^{1}H NMR spectra. [e] Determined by GPC using a polystyrene standard. [f] Measured in $CHCl_3$ at 23 °C (*c* 1.0).

trimethylene tether (Figure 1). Here two kinds of connections are possible according to the newly formed chiral center on the C2 atom, i.e., (1*S*,2*R*)-2-hydroxymethyl-1-cyclohexanol (**a**) and (1*S*,2*S*)-2-hydroxymethyl-1-cyclohexanol (**b**). The trimethylene tether of chiral templates **a** and **b** should forbid one of the three conformers of (*S*)-1,3-butanediol (**c**), i.e., clockwise gauche (g^+), anti (a), and counterclockwise gauche (g^-) forms.

In this paper, we report the difference in optical activity of polymer **3** between the radical cyclocopolymerizations of bis(4-vinylbenzoate)s having **a** and **b** templates with styrene. The chirality induction was characterized by means of the chiroptical property measurement of polymer **3**. The difference in chirality induction efficiency among chiral templates **a**−**c** was examined in terms of the conformational restriction by the trimethylene tether.

Results and Discussion

Cyclocopolymerization. The copolymerizations of (1*S*,2*R*)-2-(4-vinylbenzoyloxymethyl)-1-cyclohexyl 4-vinylbenzoate (**1a**) and (1*S*,2*S*)-2-(4-vinylbenzoyloxymethyl)-1-cyclohexyl 4-vinylbenzoate (**1b**) with styrene were carried out using 2,2′-azobis(2-methylpropionitrile) (AIBN) in toluene at 60 °C (Scheme 1 and Table 1). To calculate the monomer reactivity ratio by applying the steady-state approximation, the polymer yields were intentionally suppressed. All polymerizations proceeded homogeneously to yield polymers **2a**,**b**, which were soluble in chloroform and tetrahydrofuran. Figure 2 shows the expanded ^{13}C NMR spectra of monomers **1a**,**b** and polymers **2a**,**b**. The signals at 117 and 136 ppm due to the methine and the methylene carbons of the vinyl groups completely disappeared in the spectra of polymers **2a**,**b**, indicating that polymers **2a**,**b** consisted of cyclic repeating units (M_1) together with styrene units (M_2). The results indicate that the rigid cyclic structure in templates **a** and **b** apparently did not affect the cyclization tendency. The mole fraction of M_1 in polymer **2** (f_1), which was estimated by the area ratio between the aromatic and methyl ester regions in the ^{1}H NMR spectra of the polymer **3** (Figure 3), varied from 0.30 to 0.98 for **2a** and from 0.34 to 0.99 for **2b**. The values of the number-average molecular weight (M_n) ranged from 3300 to 31 700 for **2a** and from 2800 to 27 000 for **2b**. The Kelen−Tüdös plots[5] gave monomer reactivity ratios

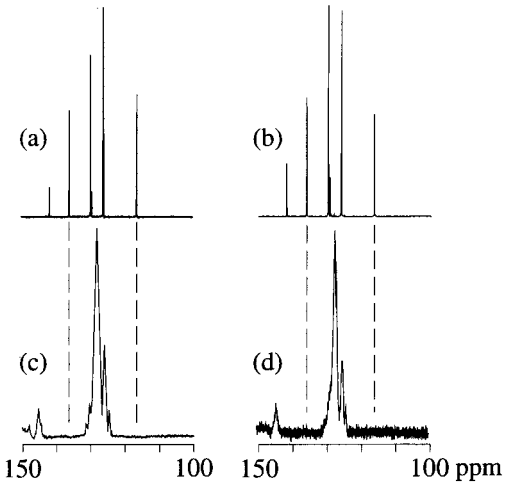


Figure 2. Expanded ^{13}C NMR spectra of monomers **1a** (a) and **1b** (b) and polymers **2a** ($f_1 = 0.30$) (c) and **2b** ($f_1 = 0.34$) (d).

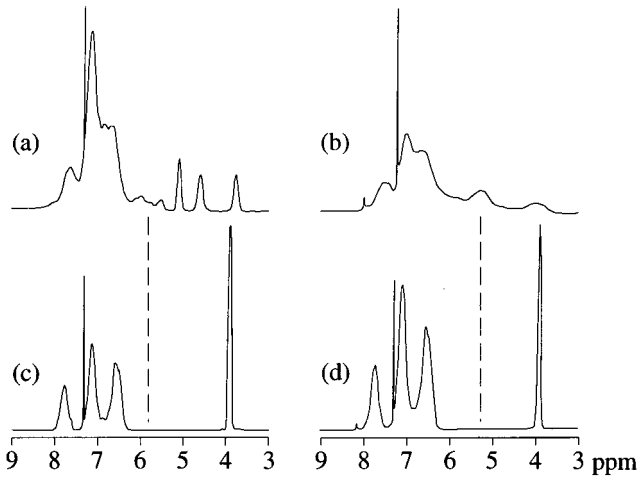


Figure 3. Expanded ^1H NMR spectra of polymers **2a** ($f_1 = 0.30$) (a) and **2b** ($f_1 = 0.34$) and its template-free polymers **3a** (c) and **3b** (d).

of $r_1 = 3.45$ and $r_2 = 0.31$ for **1a** and $r_1 = 3.22$ and $r_2 = 0.14$ for **1b**.

Template-Free Polymers 3. The removal of the chiral template from polymer **2** was performed by alkali hydrolysis using potassium hydroxide in methanol, and then the hydrolyzed polymer was treated with diazomethane to yield polymer **3**. Table 1 lists the results of the synthesis and the characteristics of polymer **3**. The M_n values ranged from 3800 to 38 200 for **3a** and from 4300 to 30 200 for **3b**. Figure 3 shows the ^1H NMR spectra of polymers **2a**,**b** and polymers **3a**,**b**. The chiral template was completely removed from polymers **2a**,**b**, because the signals at 4.0−6.0 ppm due to the template entirely disappeared.

Chiroptical Properties. The specific rotation ($[\alpha]_{435}$, *c* 1.0, $CHCl_3$) changed from +215° to +387° for **2a** and from +169° to +270° for **2b**. After the complete removal of the template, the resulting polymers **3a**,**b** showed specific rotations with a sign opposite to those for **2a**,**b** for every composition. The $[\alpha]_{435}$ values increased with a decrease in f_1 and changed from 0° to −32° for **3a** and from 0° to −18° for **3b**. Hence, both templates **a** and **b** possess the ability for the chirality induction into the polymer main chain, as well as template **c**.[4c] Figure 4 shows the specific rotations of polymers **3** divided by

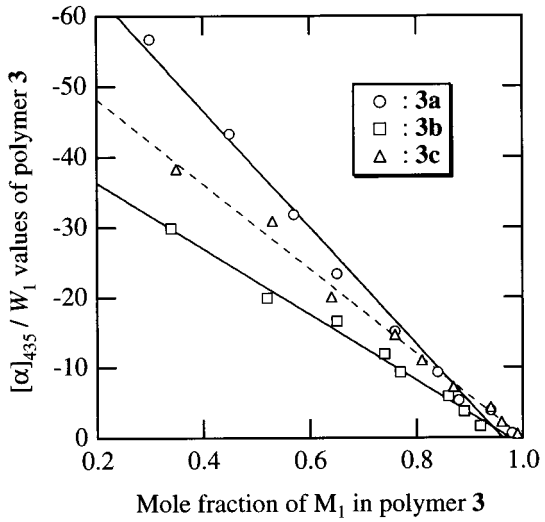


Figure 4. Plots of specific rotation of polymer **3** per one benzoate diad ($[\alpha]_{435}/W_1$) versus mole fraction of M_1 unit in the polymer **3**. W_1 means the weight fraction of M_1 unit in the polymer **3**.

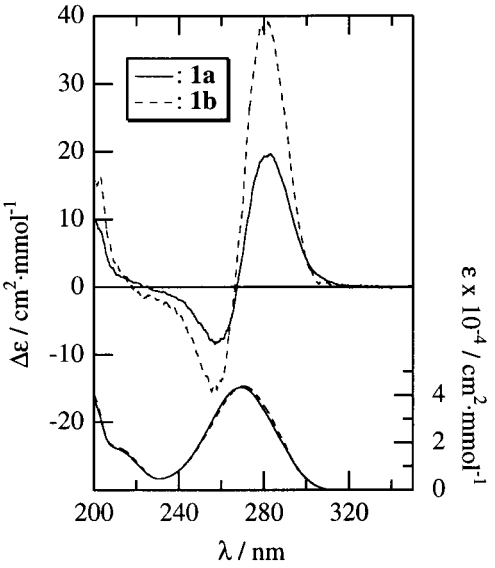


Figure 5. CD (upper) and UV (lower) spectra of monomers **1a** (solid line) and **1b** (broken line).

the weight fraction of M_1 unit ($[\alpha]_{435}/W_1$) as a function of the polymer composition (f_1). The $[\alpha]_{435}/W_1$ values remarkably increase with a decrease in f_1, indicating that the origin of the chirality in polymer **3** is attributable to the isolated benzoate diad (i.e., $M_2M_1M_2$ sequence). This fact is consistent with the concept established in the asymmetric cyclocopolymerization using a chiral template.[3] The efficiency of chirality induction, which can be estimated by the $[\alpha]_{435}/W_1$ value, for template **a** was twice that for template **b**.

Figure 5 shows the CD and UV spectra of monomers **1a**,**b**. The CD spectrum of **1a** exhibits a typical split Cotton effect with a positive first one at 281 nm and a negative second one at 259 nm. Similarly, the monomer **1b** showed a split Cotton effect with a positive first one at 282 nm and a negative second one at 256 nm. According to the exciton chirality method,[6] two 4-vinylbenzoyl groups in both **1a** and **1b** are twisted clockwise regardless of the absolute configuration on the hydroxymethyl group in templates **a** and **b**.[7] The CD spectra of polymer **3a** also exhibits a typical split Cotton

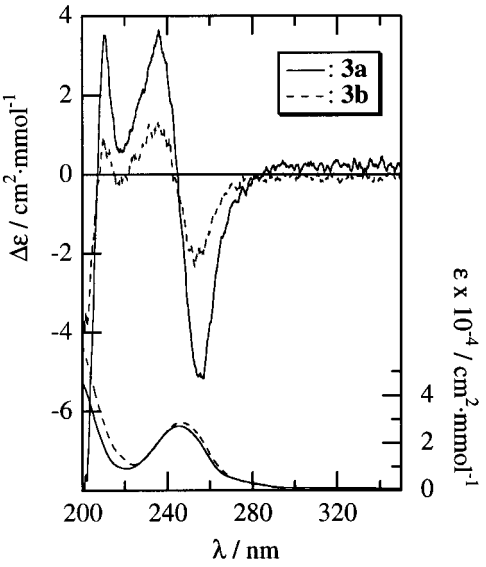


Figure 6. CD (upper) and UV (lower) spectra of polymers **3a** (f_1 = 0.30, solid line) and **3b** (f_1 = 0.34, broken line). The $\Delta\epsilon$ and ϵ values were based on the concentration of the methyl benzoate diad unit.

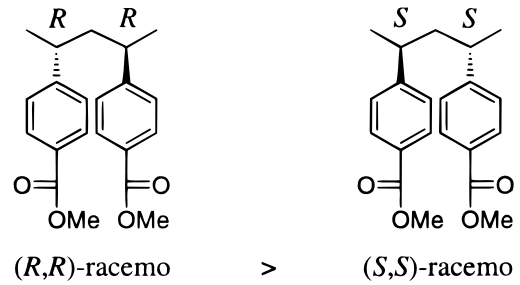


Figure 7. Enantiomeric racemo configuration of methyl benzoate diad.

effect with a negative first one at about 235 nm and a positive second one at about 253 nm (Figure 6). The split Cotton effect of **3b** is similar to that of **3a**. Contrary to monomers **1a**,**b**, polymers **3a**,**b** possess a negative chirality in which the two 4-vinylbenzoyl groups are twisted counterclockwise, indicating that polymers **3a**,**b** consist of a high content of the (*R*,*R*)-racemo benzoate diad over the (*S*,*S*)-racemo one (Figure 7).[4c] Hence, monomers **1a** and **1b** transmitted their positive chirality to a negative chirality on the polymer main chain by forming an (*R*,*R*)-racemo benzoate diad during cyclization. The *A* value, which is defined as the amplitude of the Cotton effect, of polymer **3a** was almost double that of polymer **3b**. This result is in harmony with the specific rotation of polymer **3**, indicating that the extent of preferential formation of the (*R*,*R*)-racemo benzoate diad in **1a** is higher than that in **1b**.

Conformational Effect. The $[\alpha]_{435}/W_1$ values in Figure 4 indicate that the chirality induction efficiency increased in the order of **1b** < **1c** < **1a**. To discuss the structural effect of chiral templates **a**−**c** on the chirality induction ability, we consider that both templates **a** and **b** are the conformationally restricted models of (*S*)-1,3-butanediol (i.e., template **c**) by means of the connection between the C2 and C4 positions with the trimethylene tether (Figure 1). However, the conformational restriction in template **a** differs from that in template **b** because the absolute configuration on the C2 position of template **a** differs from that of template **b**. Figure 8 shows the conformer distribution on the dihedral angle of C1−C2−C3−C4 for templates **a**−**c**. The molecular mechanics calculation (MM2 force field) indicates that the conformer of template **c** distributes into a clockwise gauche form ("g^+"), an anti form ("a"), and a counterclockwise gauche form ("g^-") at the rate of 19, 81, and 0%, respectively.[8] For template **a**, the conformer distributes into only the "a" and "g^-" forms because the tether forbids taking the "g^+" form. The equilibrium distribution between the "a" and "g^-" forms should be strongly shifted toward the "a" form because the "g^-" form of template **a** sets up two substituents on the axial position of the cyclohexane ring. On the other hand, the tether of template **b** forbids taking the "g^-" form so that the conformer distributes into only the "g^+" and "a" forms. Contrary to template **a**, both the "g^+" and "a" forms have one of the substituents on the axial position of the cyclohexane ring. Because the cyclic structure of template **b** moderates the difference in the stability

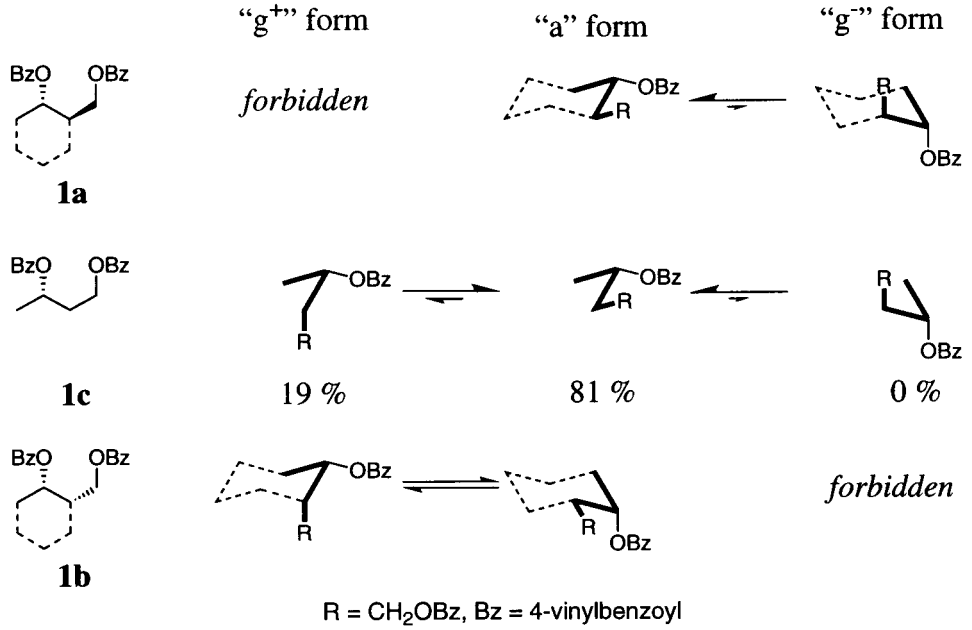


Figure 8. Geometrical restriction effect on the conformation around C1−C2−C3−C4.

between the "g^+" and "a" forms, the conformer of template **b** distributes into the "g^+" and "a" forms. The order of the narrowness of conformer distribution might concur with the order of the ability for chirality induction (i.e., **b** < **c** < **a**). For the chiral template having the (*S*)-1,3-butanediol skeleton, hence, the key to enhancement of chirality induction is to suppress the extent of the "g^+" form. Here the "g^+" and "a" forms in the C1−C2−C3−C4 skeleton mean the "g^-" and "g^+" forms in the C1−C2−C3−OBz skeleton, respectively. In other words, the key to enhancement of chirality induction is to set up a biased distribution between the two enantiomorphic gauche forms in the C1−C2−C3−OBz skeleton.

Consequently, the conformational flexibility of the carbon skeleton of the 1,3-diol template plays an important role in chirality induction. These findings indicate that the design of a tether having a suitable geometry to restrict the conformation is essential to improve the chirality induction efficiency.

Conclusions

The cyclocopolymerizations of (1*S*,2*R*)-2-(4-vinylbenzoyloxymethyl)-1-cyclohexyl 4-vinylbenzoate and (1*S*,2*S*)-2-(4-vinylbenzoyloxymethyl)-1-cyclohexyl 4-vinylbenzoate (**1a** and **1b**, respectively) with styrene were carried out to estimate the conformational effect by comparison with their acyclic model, i.e., (*S*)-1,3-butanediyl 4-vinylbenzoate (**1c**). After removal of the chiral template, the resulting polymers **3a**,**b** exhibited optical activity, indicating the chirality induction into the polymer main chain. The chirality induction efficiency increased in the order of **1b** < **1c** < **1a**. Both of the chiral templates **a** and **b** can be regarded as conformational restricted models of the chiral template **c**, and the order of chirality induction efficiency indicated that the key for chirality induction is to set up a biased distribution into the appropriate conformer.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-EX270 and JNM-A400II instruments at 30 °C in $CDCl_3$ (100 mg mL^{-1}). FD-MS was recorded on a JEOL JMS-SX102A mass spectrometer (GC-MS & NMR Laboratory, Faculty of Agriculture, Hokkaido University). The reaction for optical resolution was monitored by gas chromatography (Shimadzu GC-14A) equipped with a capillary column (Shimadzu, CBP5-M-50-025). Enantiomeric excesses (% ee) were determined by HPLC (Yanaco L-4000 W) equipped with a cellurose-tris(3,5-dimethylphenylcarbamate) column (Daicel CHIRALCEL OD) and an RI detector (Erma Optical Works, Ltd. ERC-7520). The molecular weight of the resulting polymers was measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Jasco GPC-900 system equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight (M_n) was calculated on the basis of a polystyrene calibration. Optical rotations were measured using a Jasco DIP-1000 digital polarimeter. CD spectra were measured at 21 °C in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with a 0.5 cm path length using a Jasco J-720 spectropolarimeter.

Materials. Ethyl (±)-*trans*- and *cis*-2-hydroxy-1-cyclohexanecarboxylates were prepared according to a literature procedure.[9] 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol. Dry toluene was purchased from Kanto Chemical Co. and used without further purification. Pyridine was distilled over CaH_2. HFIP was donated by Central Glass Co. and used without further purification. The seamless cellulose tube (UC24-32-100) was purchased from Viskase Sales Co. *Pseudomonas capacia lipase* (Lipase PS) was donated by Amano Pharmaceutical Co., Ltd., Japan, and used without further purification.

Ethyl (1*S*,2*S*)-2-Hydroxy-1-cyclohexanecarboxylate. Optical resolution of the preparative scale for ethyl (±)-*trans*-2-hydroxy-1-cyclohexanecarboxylate was performed by the lipase-catalyzed transesterification with vinyl acetate in *tert*-butyl methyl ether (*t*-BuOMe).[10] The procedure is as follows: A mixture of ethyl (±)-*trans*-2-hydroxy-1-cyclohexanecarboxylate (14.0 g, 81.8 mmol), vinyl acetate (7.07 g, 27.9 mmol), and lipase PS (2.20 g) in *t*-BuOMe (164 mL) was shaken at 40 °C at 150 rpm, until the unreacted substrate had become 50% as judged by GC analysis (19.5 h). After lipase was filtered off, the filtrate was concentrated and purified by column chromatography on the silica gel with hexane/ethyl acetate (volume ratio 5/1) to give ethyl (1*S*,2*S*)-2-hydroxy-1-cyclohexanecarboxylate as an unreacted substrate. The absolute configuration was assigned on the basis of the specific rotation. Yield, 7.0 g (50%, >99% ee[11]). $[\alpha]^{23}_D = +45.9°$ (*c* 1.0, $CHCl_3$) (lit.[12] $[\alpha]^{20}_D = +43°$ (*c* 5, $CHCl_3$) for 94% ee).

Ethyl (1*S*,2*R*)-2-Hydroxy-1-cyclohexanecarboxylate. Optical resolution of ethyl (±)-*cis*-2-hydroxy-1-cyclohexanecarboxylate was performed by the same method as that for the trans isomer. The mixture of ethyl (±)-*cis*-2-hydroxy-1-cyclohexanecarboxylate (20.0 g, 117 mmol), vinyl acetate (10.3 g, 0.12 mol), and lipase PS (9.4 g) in *t*-BuOMe (230 mL) was shaken at 40 °C at 150 rpm (about 46 h). The reaction mixture obtained was purified by column chromatography on silica gel with hexane/ethyl acetate (volume ratio 3/1) to give ethyl (1*S*,2*S*)-2-hydroxy-1-cyclohexanecarboxylate as an unreacted substrate. Yield, 7.0 g (50%, >99% ee[11]). $[\alpha]^{23}_D = +22.1°$ (*c* 1.0, $CHCl_3$) (lit.[9] $[\alpha]^{25}_D = +18.8°$ (*c* 0.69, $CHCl_3$) for >99% ee).

(1*S*,2*R*)-2-Hydroxymethyl-1-cyclohexanol (a). To a solution of ethyl (1*S*,2*S*)-2-hydroxy-1-cyclohexanecarboxylate (2.4 g, 15 mmol) in ethanol (7.5 mL), sodium borohydride (0.57 g) was gradually added and stirred overnight at room temperature. After the starting material was consumed by TLC analysis, acetic acid was added dropwise to deactivate the residual sodium borohydride. After the reaction mixture was concentrated under reduced pressure, the inorganic salt was removed from the residue by short column chromatography on alumina with ethyl acetate. The filtrate was further purified by column chromatography on silica gel with ethyl acetate to give (1*S*,2*R*)-2-hydroxymethyl-1-cyclohexanol as a colorless viscous liquid. Yield, 1.6 g (92%). $[\alpha]^{23}_D = 5.9°$, $[\alpha]^{23}_{435} = 13.4°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.23 (s, 1H, −OH), 4.15 (s, 1H, −OH), 3.70−3.58 (m, 2H, $-O-CH_2-$), 3.51−3.45 (m, 1H, −O−CH⟨), 1.96−0.86 (m, 8H, $-CH_2-$). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) = 68.2 (OCH), 65.1 (OCH_2), 45.9 (CH), 35.1, 27.2, 25.0, 24.4 (CH_2). FD-MS: m/z = 130 (M^+).

(1*S*,2*S*)-2-Hydroxymethyl-1-cyclohexanol (b). The same procedure as that for **a** was applied to ethyl (1*S*,2*R*)-2-hydroxy-1-cyclohexanecarboxylate (2.4 g, 15 mmol), ethanol (7.5 mL), and sodium borohydride (0.57 g). After the purification, (1*S*,2*S*)-2-hydroxymethyl-1-cyclohexaol was obtained as a colorless viscous liquid. Yield, 1.6 g (92%). $[\alpha]^{23}_D = 31.0°$, $[\alpha]^{23}_{435} = 62.1°$(*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.27 (s, 1H, −OH), 4.10 (m, 1H, −O−CH⟨), 3.97 (s, 1H, −OH) 3.70−3.60 (m, 2H, $-O-CH_2-$), 1.80−1.26 (m, 8H, $-CH_2-$). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) = 68.7 (OCH), 65.1 (OCH_2), 42.4 (CH), 32.5, 24.8, 23.4, 20.4 (CH_2). FD-MS: m/z = 130 (M^+).

(1*S*,2*R*)-2-(4-Vinylbenzoyloxymethyl)-1-cyclohexyl 4-Vinylbenzoate (1a). A solution of **a** (2.6 g, 20 mmol) in dry pyridine (130 mL) was cooled to 5 °C in an ice bath. 4-Vinylbenzoyl chloride (10.0 g, 60.0 mmol) was gradually added to this solution so that the temperature of the solution did not rise above 10 °C. After the addition, the reaction mixture was stirred overnight at room temperature. The mixture was diluted with water (130 mL), and then stirring was continued for 1 h. After the mixture was extracted with diethyl ether (3 × 150 mL), the organic layer was washed with several portions of 1 N HCl, aqueous sodium hydroxide, and water and dried over anhydrous sodium sulfate. After the removal of the solvent under reduced pressure, the residue was purified by column chromatography on alumina with hexane/ether (vol-

ume ratio 4:1) to give white solid of **1a**. Yield, 6.9 g (88%). $[\alpha]^{23}_{D} = +148°$, $[\alpha]^{23}_{435} = +338°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.97 (d, ^3J = 8.5 Hz, 2H, Ar), 7.94 (d, ^3J = 8.5 Hz, 2H, Ar), 7.40 (d, ^3J = 8.3 Hz, 2H, Ar), 7.38 (d, ^3J = 8.3 Hz, 2H, Ar), 6.73 (dd, $^3J_{trans}$ = 17.7 Hz, $^3J_{cis}$ = 11.0 Hz, 1H, =CH−), 6.72 (dd, $^3J_{trans}$ = 17.6 Hz, $^3J_{cis}$ = 11.0 Hz, 1H, =CH−), 5.84 (dd, $^3J_{trans}$ = 17.7 Hz, $^2J_{gem}$ = 0.6 Hz, 1H, =CH_2), 5.83 (dd, $^3J_{trans}$ = 17.6 Hz, $^2J_{gem}$ = 0.7 Hz, 1H, =CH_2), 5.38 (d, $^3J_{cis}$ = 11.0 Hz, 2H, =CH_2), 4.98−5.04 (m, 1H, −O−CH⟨), 4.44 (dd, ^3J = 4.4 Hz, $^2J_{gem}$ = 11.0 Hz, 1H, −O−CH_2−), 4.24 (dd, ^3J = 5.9 Hz, $^2J_{gem}$ = 11.0 Hz, 1H, −O−CH_2−), 2.19−2.23 (m, 2H, −CH_2−), 2.12−2.17 (m, 1H, CH), 1.76−1.88 (m, 2H, −CH_2−), 1.26−1.49 (m, 4H, −CH_2−). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) = 166.3, 165.7 (C=O), 141.8, 129.9, 129.8, 129.6, 129.3 (Ar), 136.0 (=CH−), 116.4 (=CH_2), 74.3 (OCH), 66.1 (OCH_2), 41.9 (CH), 31.8, 28.4, 24.8, 24.4 (CH_2). Anal. Calcd for $C_{25}H_{26}O_4$ (390.5): C, 76.90; H, 6.71. Found: C, 76.94; H, 6.82.

(1*S*,2*S*)-2-(4-Vinylbenzoyloxymethyl)-1-cyclohexyl 4-Vinylbenzoate (1b). The same procedure as that for **1a** was applied to **b** (2.6 g, 22 mmol), dry pyridine (130 mL), and 4-vinylbenzoyl chloride (14.4 g, 44 mmol). The crude product was purified by column chromatography on silica gel with hexane/ether (volume ratio 5:1) to give white crystals of **1b**. Yield, 7.1 g (83%). $[\alpha]^{23}_{D} = +146°$, $[\alpha]^{23}_{435} = +483°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.02 (d,^3J = 8.3 Hz, 2H, Ar), 8.00 (d, ^3J = 8.3 Hz, 2H, Ar), 7.43 (d, ^3J = 8.3 Hz, 2H, Ar), 7.38 (d,^3J = 8.3 Hz, 2H, Ar), 6.74 (dd, $^3J_{trans}$ = 17.7 Hz, $^3J_{cis}$ = 10.7 Hz, 1H, =CH−), 6.70 (dd, $^3J_{trans}$ = 17.8 Hz, $^3J_{cis}$ = 10.7 Hz, 1H, =CH−), 5.85 (d, $^3J_{trans}$ = 17.6 Hz, 1H, =CH_2), 5.80 (d, $^3J_{trans}$ = 17.6 Hz, 1H, =CH_2), 5.36 (d, $^3J_{cis}$ = 11.0 Hz, 1H, =CH_2), 4.98−5.04 (m, 1H, −O−CH⟨), 4.33 (dd, ^3J = 6.3 Hz, $^2J_{gem}$ = 11.0 Hz, 1H, −O−CH_2−), 4.22 (dd, ^3J = 8.1 Hz, $^2J_{gem}$ = 11.0 Hz, 1H, −O−CH_2−), 2.19−2.23 (m, 2H −CH_2−), 2.12−2.17 (m, 1H, CH), 1.76−1.88 (m, 2H −CH_2−), 1.26−1.49 (m, 4H −CH_2−) ^{13}C NMR (67.8 MHz, $CDCl_3$): δ (ppm) = 166.1, 165.3 (C=O), 141.7, 135.8, 129.7, 129.2, 128.6, 128.0 (Ar), 125.9 (=CH−), 116.2 (=CH_2), 70.0 (OCH), 65.5 (OCH_2), 39.7 (CH), 29.7, 24.6, 24.2, 20.4 (CH_2). Anal. Calcd for $C_{25}H_{26}O_4$ (390.5): C, 76.90; H, 6.71. Found: C, 76.21; H, 6.78.

Cyclocopolymerization. The copolymerization of **1** with styrene was carried out using AIBN in toluene at 60 °C. After an appropriate time, the polymerization mixture was poured into methanol and the precipitate was filtered. The obtained polymer was purified by reprecipitation with chloroform−methanol and dried in vacuo.

Synthesis of Poly[(methyl 4-vinylbenzoate)-*co*-styrene] (3). The removal of the chiral template from polymer **2** was carried out using KOH in aqueous methanol, and then the hydrolyzed copolymers were esterified by treatment with diazomethane in benzene/ether.[13]

References and Notes

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