Chirality Induction in Cyclocopolymerization. 14. Template Effect of 1,2-Cycloalkanediol in the Cyclocopolymerization of Bis(4-vinylbenzoate)s with Styrene

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Received May 17, 2000

ABSTRACT: A series of chiral 1,2-cycloalkanediols including (1*S*,2*S*)-1,2-cyclopentanediol, (1*S*,2*S*)-1,2-cyclohexanediol, (1*S*,2*S*)-1,2-cycloheptanediol, and (1*S*,2*S*)-1,2-cyclooctanediol (**a**, **b**, **c**, and **d**) were used as chiral templates in the cyclocopolymerization of bis(4-vinylbenzoate)s (**1a**−**d**) with styrene. The copolymerizations of **1a** with styrene produced an insoluble gel at a high mole fraction of **1a** in the feed. On the other hand, the copolymerization of **1b**−**d** with styrene proceeded homogeneously to yield polymers **2b**−**d**, which were soluble in chloroform and tetrahydrofuran. After the removal of the chiral template from the resulting polymers **2a**−**d**, polymers **3b**−**d** exhibited optical rotations ($[\alpha]_{435}$, *c* 1.0, $CHCl_3$) of −2.2 to −17.9° whose signs were opposite to those of polymers **2b**−**d**, while polymer **3a** showed little or no optical activity. Hence, the efficiency of templates on the chirality induction improved by expansion of the ring size of the chiral template; i.e., **1a** ≪ **1b** < **1c** < **1d**. The A values of the CD spectra of monomers **1a**−**d** related to the dihedral angle between two 4-vinylbenzoyl groups of the monomers which decreased with increasing ring size. Therefore, the results indicated that the dihedral angle affected the chiral inductivity of the template.

Introduction

Synthesis of an optically active polymer has been interesting in terms of fine control of the main chain structure. The asymmetric cyclocopolymerization offers a synthetic methodology for an optically active polymer due to the main chain chirality by forming an enantiomeric racemo diad controlled with a chiral template.[1] We have reported the synthesis of optically active poly[(methyl 4-vinylbenzoate)-*co*-styrene] through the cyclocopolymerization of bis(4-vinylbenzoate) having a chiral diol as a template with styrene, followed by removing the template.[2] Several types of templates, such as carbohydrate derivatives[3] and synthetic chiral diols,[4] have been applied to the asymmetric cyclocopolymerization in order to clarify the effect of the template on the chirality induction. For example, the effect of the distance between the two 4-vinylbenzoyl groups on chirality induction was clarified using a series of chiral templates, i.e., (2*S*,3*S*)-2,3-butanediol, (2*S*,4*S*)-2,4-pentanediol, and (2*S*,5*S*)-2,5-hexanediol.[4]

The dihedral angle between the two 4-vinylbenzoyl groups should affect the chirality induction in the cyclocopolymerization. To clarify the effect of the dihedral angle, simple 1,2-cycloalkanediols are suitable chiral templates, because the dihedral angle can be changed by the ring size but fixed by the cyclic structure.

In this paper, we report the asymmetric cyclocopolymerization of bis(4-vinylbenzoate)s of chiral 1,2-cycloalkanediols, i.e., (1*S*,2*S*)-1,2-cyclopentanediol, (1*S*,2*S*)-1,2-cyclohexanediol, (1*S*,2*S*)-1,2-cycloheptanediol, and (1*S*,2*S*)-1,2-cyclooctanediol (**a**, **b**, **c**, and **d**, respectively) with styrene (Scheme 1). The chirality induction was confirmed by chiroptical measurement of the template-free polymer. The difference in the ring size of these chiral templates offered the characteristics of chirality induction in terms of the dihedral angle between the two 4-vinylbenzoyl groups.

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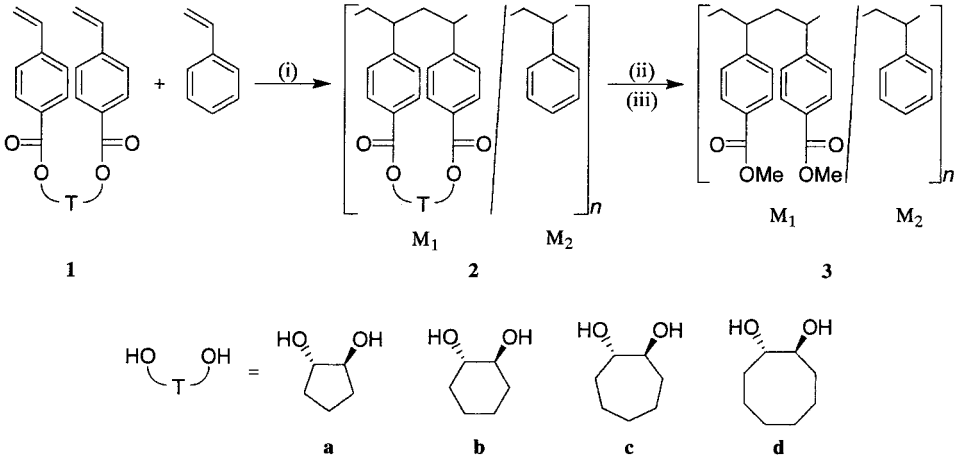
Results and Discussion

Cyclocopolymerization. The copolymerizations of bis(4-vinylbenzoate)s of 1,2-cycloalkanediols (**1a**−**d**) (M_1) with styrene (M_2) were carried out using 2,2′-azobis(2-methylpropionitrile) (AIBN) in dry toluene at 60 °C under a nitrogen atmosphere (Scheme 1 and Table 1). The polymerization of **1a** with styrene produced an insoluble gel when the mole fraction of **1a** in the feed exceeded 0.7. On the other hand, the polymerizations of monomers **1b**−**d** with styrene proceeded homogeneously to yield polymers **2b**−**d**, which were soluble in chloroform and tetrahydrofuran. Figure 1B shows the quantitative ^{13}C NMR spectra of the resulting polymer. The mole fraction of the M_1 unit in polymer **2** (f_1), which was estimated by the area ratio between the aromatic (123−131 ppm) and the carbonyl (164−168 ppm) regions in the quantitative ^{13}C NMR spectrum, was higher than that of **1a**−**d** in the feed (F_1). Hence the polymerization reactivity of **1a**−**d** is higher than that of styrene. The extent of cyclization (f_c), which was determined by the area ratio between the vinyl (117 and 136 ppm) and the carbonyl (164−168 ppm) regions in the quantitative ^{13}C NMR spectrum, generally increased with decreasing F_1.

The expression of Roovers and Smets for the extent of cyclization (eq 8),[5] which was obtained from a set of elementary reactions in the cyclocopolymerization

10.1021/ma000853b CCC: $20.00
Published on Web 12/08/2000

Scheme 1. Cyclocopolymerization of Bis(4-vinylbenzoate)s of 1,2-Cycloalkanediols (1a−d) with Styrene



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

Table 1. Copolymerizations of Bis(4-vinylbenzoate)s (1a−d) with Styrene To Form Poly[(methyl 4-vinylbenzoate)-*co*-styrene] (3a−d)

	polymer **2**[a]							polymer **3**[b]		
monomer	F_1[c]	time, h	yield, %	f_1[d]	f_c[e]	$M_n \times 10^{-3}$ (M_w/M_n)[f]	$[\alpha]_{435}$[g], deg	yield, %	$M_n \times 10^{-3}$ (M_w/M_n)[f]	$[\alpha]_{435}$[g], deg
1a	0.6	3.5	26	0.75	0.49	11.8 (32.1)	+386	57	8.2 (1.67)	+0.9
	0.4	4.8	22	0.64	0.64	9.3 (4.34)	+371	54	5.3 (2.07)	−0.2
	0.2	11.0	21	0.42	0.73	5.1 (2.28)	+315	62	3.0 (1.98)	+0.5
	0.1	20.0	28	0.26	0.75	4.2 (2.12)	+251	30	3.5 (1.56)	+0.2
1b	0.6	4.0	27	0.65	0.91	10.0 (2.46)	+392	51	11.9 (1.56)	−2.2
	0.4	4.0	11	0.61	0.87	6.4 (2.64)	+377	75	9.3 (1.56)	−3.0
	0.2	9.5	27	0.39	0.93	4.2 (1.95)	+340	66	5.2 (1.52)	−5.9
	0.1	14.5	22	0.26	0.90	3.7 (1.77)	+291	35	4.0 (2.41)	−7.2
1c	0.6	3.5	25	0.76	0.93	10.5 (2.55)	+360	55	14.1 (1.47)	−2.8
	0.4	5.0	28	0.61	0.91	7.6 (2.23)	+347	60	6.5 (2.21)	−4.7
	0.2	7.0	30	0.40	0.91	3.7 (2.01)	+320	65	3.6 (1.89)	−10.4
	0.1	15.0	24	0.27	1.00	2.9 (2.06)	+274	81	3.3 (1.65)	−13.1
1d	0.6	5.5	14	0.82	0.96	9.7 (2.36)	+336	21	14.0 (2.30)	−3.0
	0.4	5.2	16	0.67	0.97	6.1 (2.57)	+325	16	10.9 (2.00)	−7.8
	0.2	7.0	20	0.40	0.98	4.3 (2.10)	+304	69	4.1 (1.93)	−11.9
	0.1	14.5	22	0.25	1.00	2.3 (2.28)	+256	22	3.6 (1.76)	−17.9

[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 quantitative ^{13}C NMR spectra. [e] Extent of cyclization determined by quantitative ^{13}C NMR spectra. [f] Determined by GPC using polystyrene standards. [g] Measured in $CHCl_3$ at 23 °C (*c* 1.0).

(eq 1 ∼ 7), can be applied to verify the cyclization tendency of monomers **1a**−**d**.

$$M_1^{\bullet} + M_1 \rightarrow M_1^{\bullet} \quad k_{11} = [M_1^{\bullet}]/[M_1] \tag{1}$$

$$M_1^{\bullet} + M_2 \rightarrow M_2^{\bullet} \quad k_{12} = [M_1^{\bullet}]/[M_2] \tag{2}$$

$$M_1^{\bullet} \rightarrow M_c^{\bullet} \quad k_c = [M_1^{\bullet}] \tag{3}$$

$$M_c^{\bullet} + M_1 \rightarrow M_1^{\bullet} \quad k_{c1} = [M_c^{\bullet}]/[M_1] \tag{4}$$

$$M_c^{\bullet} + M_2 \rightarrow M_2^{\bullet} \quad k_{c2} = [M_c^{\bullet}]/[M_2] \tag{5}$$

$$M_2^{\bullet} + M_1 \rightarrow M_1^{\bullet} \quad k_{21} = [M_2^{\bullet}]/[M_1] \tag{6}$$

$$M_2^{\bullet} + M_2 \rightarrow M_2^{\bullet} \quad k_{22} = [M_2^{\bullet}]/[M_2] \tag{7}$$

$$\frac{1}{f_c} = 1 + 2\frac{[M_1]}{K_c} + \frac{[M_2]}{K_c'} \tag{8}$$

In these equations, $K_c = k_c/k_{11}$, $K_c' = k_c/k_{12}$, and f_c is the extent of cyclization, and $[M_1]$ and $[M_2]$ are the concentrations of the two monomers in the feed. Substitution of the expression $[M_1]$ and $[M_2]$ yields

$$\frac{1}{f_c} = \left(1 + \frac{c}{K_c'}\right) + \left(2\frac{c}{K_c} - \frac{c}{K_c'}\right)F_1 \tag{9}$$

where *c* is the total monomer concentration (here, *c* = 0.1 mol·L^{-1}). Table 2 lists the K_c and K_c' values, which were obtained by plotting of the reciprocal value of f_c against the value of F_1. The K_c value of monomer **1d** is comparable to 2.3 mol·L^{-1} for 1,2:5,6-di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol.[6] The K_c and K_c' values increase from 0.2 to 2.6 mol·L^{-1} and from 0.8 to >8.6 mol·L^{-1}, respectively, as the ring size of the chiral template expands, i.e., **a** ≪ **b** < **c** < **d**, indicating that the cyclization tendency of bis(4-vinylbenzoate) of 1,2-cycloalkanediol was remarkably improved by expansion of the ring size. Monomer **1a** has a considerably lower cyclopolymerization tendency than the other monomers. This is attributed to the rigid conformation of the five-membered ring having a large dihedral angle between the two polymerizable groups. The molecular mechanics calculation (MM2 force field[7]) also indicates that the

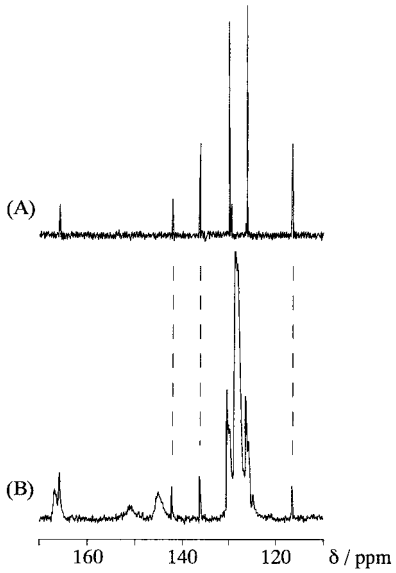


Figure 1. (A) ^{13}C NMR spectrum of monomer **1a** and (B) ^{13}C NMR (inverse gated decoupling) spectrum of polymer **2a** (f_1 = 0.26, f_c = 0.75).

Table 2. K_c and K_c' Values[a]

monomer	K_c, mol·L^{-1}	K_c', mol·L^{-1}
1a	0.2	0.8
1b	1.6	1.0
1c	1.4	3.0
1d	2.6	>8.6[b]

[a] These values were calculated by eq 9. [b] The calculated K_c' value is larger than the styrene bulk concentration (8.6 mol·L^{-1}).

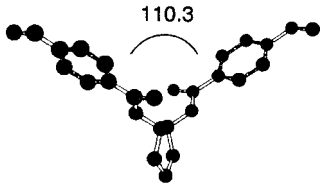


Figure 2. Geometry of **1a** optimized using MM2 force field.

conformational distribution of **1a** is quite narrow with a dihedral angle of 110.3° (Figure 2).

Template-Free Polymers. To confirm the chirality induction in the polymer main chain, the removal of the chiral template was carried out by alkaline hydrolysis using potassium hydroxide in methanol, and then the hydrolyzed polymer was treated with diazomethane. Figure 3 shows the expanded ^1H NMR spectra of polymers **2** and **3**. Because the signals at 4.5−6.0 ppm due to the chiral template disappeared entirely, the chiral template was completely removed. Hence, polymers **3** were assigned to poly[(methyl 4-vinylbenzoate)-*co*-styrene].

Chiroptical Properties. As the F_1 value increased from 0.1 to 0.6, the specific rotation ($[\alpha]_{435}$, *c* 1.0, $CHCl_3$) of polymers **2** changed from +251 to +386° for **2a**, from +291 to +392° for **2b**, from +274 to +360° for **2c**, and from +256 to +336° for **2d**. After the complete removal of the chiral template, the specific rotations ($[\alpha]_{435}$, *c* 1.0, $CHCl_3$) for **3a** were nearly 0°, i.e., in the range of −0.5 to +0.9°. On the other hand, **3b**−**d** showed specific rotations with a sign opposite to those for polymers **2b**−**d**. The specific rotations changed from −2.2 to −7.2° for **3b**, from −2.8 to −13.1° for **3c**, and from −3.0 to −17.9° for **3d**. The specific rotation of **3** depends on the stereoselectivity in the cyclization as well as on the

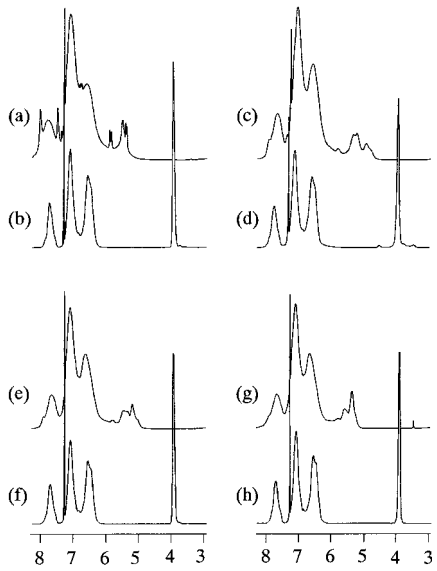


Figure 3. ^1H NMR spectra of polymers **2a**−**d** and **3a**−**d**: (a) **2a** and (b) **3a** (f_1 = 0.26, f_c = 0.75); (c) **2b** and (d) **3b** (f_1 = 0.26, f_c = 0.89); (e) **2c** and (f) **3c** (f_1 = 0.27, f_c = 1.00); (g) **2d** and (h) **3d** (f_1 = 0.25, f_c = 1.00).

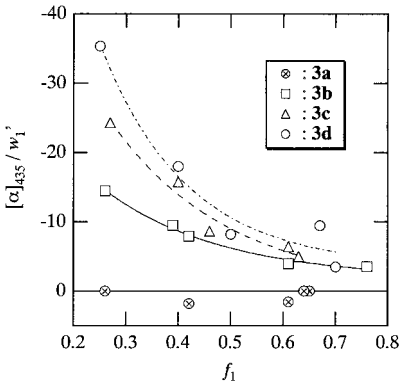


Figure 4. Specific rotations of polymers **3** ($[\alpha]_{435}$) divided by the w_1' value as a function of the polymer composition (f_1).

extent of cyclization because the chirality induction should occur through the intramolecular cyclization of monomer **1**. To remove the effect of the difference in the f_c values, the weight fraction of the benzoate diad derived from the cyclic unit (w_1') is calculated according to eq 10.

$$w_1' = \frac{324 f_1 f_c}{324 f_1 f_c + 162 f_1(1 - f_c) + 104(1 - f_1)} \quad (10)$$

Figure 4 shows the specific rotations of polymers **3** divided by the w_1' as a function of the polymer composition (f_1). The $[\alpha]_{435}/w_1'$ value, which is the relative efficiency of the chirality induction in the intramolecular cyclization of monomer **1**, increases significantly with decreasing f_1. This means that the optical activity is attributable to the benzoate diad isolated by styrene units. Figure 4 also indicates that the efficiency for chirality induction increases in the order, **3a** ≪ **3b** < **3c** < **3d**.

Figure 5 shows the CD and UV spectra of monomers **1a**−**d**. The CD spectra show a split Cotton effect with a positive first Cotton effect ($\Delta\epsilon_1$) and a negative second one ($\Delta\epsilon_2$). According to the CD exciton chirality method,[8] these CD spectra indicate that two benzoate chromophores of monomers **1a**−**d** twist clockwise, as expected

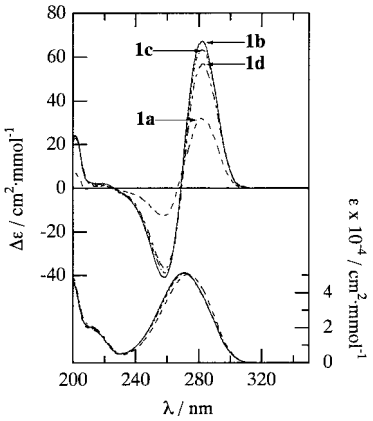


Figure 5. CD and UV spectra of monomers **1a**−**d**.

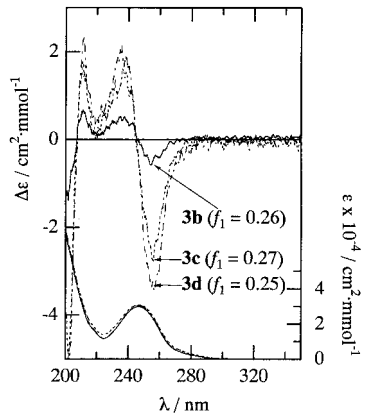


Figure 6. CD and UV spectra of polymers **3a**−**d**.

from the chiral template configuration. Except for polymer **3a**, the CD spectra of polymers **3b**−**d** (Figure 6) also showed a split Cotton effect with a negative first Cotton effect and a positive second one, in which the signs of the Cotton effect were opposite to those of monomers **1b**−**d** (Figure 5). Thus, polymers **3b**−**d** have a negative chirality, in which two vicinal benzoate units twist counterclockwise. Hence polymers **3b**−**d** possess a segmental distribution with a higher content of (*R*,*R*)-racemo benzoate diad than that of the (*S*,*S*)-racemo one. The *A* values, which are defined as the amplitude of the split Cotton effect (i.e., the absolute value of $\Delta\epsilon_1 - \Delta\epsilon_2$), are also a suitable index for the extent of preferential formation of the (*R*,*R*)-racemo benzoate diad in polymers **3**. The A values were 0 for **3a**, 1.1 for **3b**, 4.4 for **3c**, and 5.3 for **3d**. Therefore, the extent of the preferential formation of the (*R*,*R*)-racemo benzoate diads over the (*S*,*S*)-racemo one increases in the order, **3a** ≪ **3b** < **3c** < **3d**, consistent with the specific rotations of polymers **3a**−**d**. These results indicate that the increase in the ring size of the 1,2-cycloalkanediol templates certainly enhanced the efficiency of chirality induction in the polymer main chain.

Ring Size Effect. According to the theoretical calculation of exciton coupling in a vicinal glycol system,[8] the *A* value of the split Cotton effect reaches a maximum in the dihedral angle θ between the two chromophores of ca. 70° and decreases to zero as the dihedral angle θ decreases to 0° or increases to 180°. Because monomer **1b** should have two 4-vinylbenzoyl groups at the equatorial position, the dihedral angle θ is approximately equal to 60°. For the bis(4-vinylbenzoate)s derived from six-, seven-, and eight-membered 1,2-cycloalkanediols, the *A* values decrease with increasing ring size, i.e., in

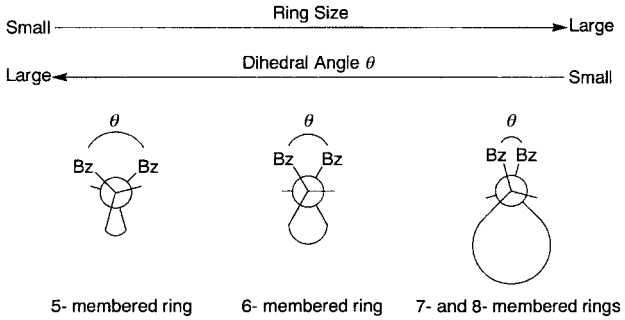


Figure 7. Summary of the ring size effect.

the order **1b** > **1c** > **1d**, suggesting a decrease in the dihedral angle θ (Figures 5 and 7). For the bis(4-vinylbenzoate) of five-membered 1,2-cycloalkanediol (**1a**), the *A* value is much lower than that of **1b**. On the other hand, the low extent of cyclization in **1a** means that their two 4-vinylbenzoyl groups should be far from each other. Hence the low *A* value of **1a** should be due to its larger dihedral angle θ compared to **1b**. The change in the ring size of 1,2-cycloalkanediols altered the dihedral angle θ between two 4-vinylbenzoyl groups, and consequently, the increase in the ring size led to a decrease in the dihedral angle θ (Figure 7). Here the order of the chirality induction, i.e. **1a** ≪ **1b** < **1c** < **1d**, corresponds to the reverse order of the dihedral angle θ. Therefore, the smaller dihedral angle θ between two 4-vinylbenzoyl groups is preferable to induce chirality into the polymer main chain.

Conclusions

The cyclocopolymerization of (1*S*,2*S*)-1,2-cyclopentanediyl, (1*S*,2*S*)-1,2-cyclohexanediyl, (1*S*,2*S*)-1,2-cycloheptanediyl, and (1*S*,2*S*)-1,2-cyclooctanediyl bis(4-vinylbenzoate)s (**1a**−**d**, respectively) with styrene was carried out to examine the effect of the dihedral angle between the two 4-vinylbenzoyl groups on the chirality induction. The extent of cyclization of polymer **2** improved with increasing ring size of the 1,2-cycloalkanediol of monomer **1**. After removal of the chiral template, polymers **3b**−**d** showed a specific rotation with a sign opposite to those of polymers **2b**−**d**, while polymer **3a** showed little or no optical activity. The specific rotations indicated that the chirality induction efficiency increases on the order of **3a** ≪ **3b** < **3c** < **3d**. The A values for the CD spectra of monomers **1a**−**d** indicated that the dihedral angle θ between the two 4-vinylbenzoyl groups decreases with increasing ring size of the 1,2-cycloalkanediols, i.e. **1a** > **1b** > **1c** > **1d**. For the synthesis of an optically active polymer through the cyclocopolymerization of bis(4-vinylbenzoate) with styrene, therefore, the *periplanar* conformation between the two 4-vinylbenzoyl groups has the advantage of chirality induction as well as cyclization.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-EX270 and JNM-A400II instruments. Quantitative ^{13}C NMR spectra were obtained at 30 °C in $CDCl_3$ (100 mg·mL^{-1}; delay time 7.0 s; inverse gated decoupling). The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) at 40 °C in tetrahydrofuran (1.0 mL·min^{-1}) with a Jasco GPC-900 system equipped with a set of Waters Ultrastyragel 7 μm column (linear, 7.8 mm × 300 mm) and two Shodex KF-804L columns (linear, 8 mm × 300 mm). The number-average molecular weight (M_n)

was calculated on the basis of a polystyrene calibration. Optical rotations were determined with a Jasco DIP-1000 digital polarimeter. CD spectra were measured at 22 °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. (±)-*trans*-1,2-Cyclopentanediol,[9] (±)-*trans*-1,2-cyclohexanediol,[9] (±)-*trans*-1,2-cycloheptanediol,[9] and (±)-*trans*-1,2-cyclooctanediol[10] were synthesized according to literature procedures. (1*S*,2*S*)-1,2-Cyclopentanediol, (1*S*,2*S*)-1,2-cyclohexanediol, (1*S*,2*S*)-1,2-cycloheptanediol, and (1*S*,2*S*)-1,2-cyclooctanediol (**a**, **b**, **c**, and **d**), were prepared by optical resolution of the corresponding (±)-*trans*-1,2-cycloalkanediol using *Pseudomonas capacia lipase* (Lipase PS) as a catalyst, followed by hydrolysis of the corresponding (1*S*,2*S*)-2-acetoxy-1-cycloalkanols obtained.[11] Enantiomeric excesses (% ee) of the chiral diols used as templates were 95% ee for **a**, >99% ee for **b**[12] and **c**, and 99% ee for **d**, which were based on the chiral gas chromatography (GC) analysis before hydrolysis. 4-Vinylbenzoyl chloride[13] and diazomethane[14] were synthesized according to literature procedures. Styrene (Kanto Chemical Co., >99.0%) was distilled just before use. 2,2′-Azobis(2-methylpropionitrile) (AIBN) (Kanto Chemical Co., >97%) was recrystallized from methanol. Dry toluene (Kanto Chemical Co., >99.5%) was used without further purification. Pyridine (Kanto Chemical Co., >99%) was distilled over CaH_2 just before use. HFIP was donated by Central Glass Co. and used without further purification. Seamless cellulose tubing was obtained from Viskase Sales Co. (UC24-32-100).

(1*S*,2*S*)-1,2-Cyclopentanediyl Bis(4-vinylbenzoate) (1a). The procedure is analogous to those reported in previous papars.[3] A solution of (1*S*,2*S*)-1,2-cyclopentanediol (**a**) (2.0 g, 20 mmol) in dry pyridine (100 mL) was cooled in an ice bath. While the temperature of the solution was kept below 10 °C, 4-vinylbenzoyl chloride (10 g, 60 mmol) was gradually added to the solution. After the addition, the reaction mixture was stirred overnight at room temperature. The mixture was diluted with water (125 mL) and was stirred for 1 h. The mixture was extracted three times with diethyl ether (150 mL). The extract was washed with several portions of 1 N HCl, 5% aqueous NaOH, and water and then dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with diethyl ether/hexane (volume ratio 1/4) to give **1a** as a white solid. Yield: 6.3 g (88%). $[\alpha]_{435} = +555°$, $[\alpha]_D = +224°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 7.98 (d, ^3J = 8.6 Hz, 4H, Ar), 7.45 (d, ^3J = 8.3 Hz, 4H, Ar), 6.75 (dd, $^3J_{trans}$ = 17.8 Hz, $^3J_{cis}$ = 10.9 Hz, 2H, −CH═), 5.86 (d, $^3J_{trans}$ = 17.8 Hz, 2H, ═CH_2), 5.50−5.47 (m, 2H, −O−CH<), 5.38 (d, $^3J_{cis}$ = 10.9 Hz, 2H, ═CH_2), 2.40−2.27 (m, 2H, cyclic CH_2), 1.98−1.80 (m, 4H, cyclic CH_2). ^{13}C NMR (67.7 MHz, $CDCl_3$): δ (ppm) = 165.6 (C═O), 142.0 (Ar), 130.0 (Ar), 129.2 (Ar), 126.1 (Ar), 136.0 (−CH═), 116.5 (═CH_2), 79.5 (−O−CH<), 30.5 (cyclic CH_2), 21.6 (cyclic CH_2). IR (KBr): ν (cm^{-1}) = 1712 (C═O, st), 1608 (C═C, st). Anal. Calcd for $C_{23}H_{22}O_4$ (362.4): C 76.22; H 6.12. Found: C 75.98; H 6.42.

(1*S*,2*S*)-1,2-Cyclohexanediyl Bis(4-vinylbenzoate) (1b). The same procedure as that for **1a** was applied to (1*S*,2*S*)-1,2-cyclohexanediol (**b**) (2.0 g, 17 mmol), 4-vinylbenzoyl chloride (10 g, 60 mmol), and 100 mL of pyridine. The crude product was purified by column chromatography on silica gel with diethyl ether/hexane (volume ratio 1/4) to give **1b** as a colorless sticky liquid. Yield: 5.5 g (84%). $[\alpha]_{435} = +628°$, $[\alpha]_D = +244°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, ^3J = 8.6 Hz, 4H, Ar), 7.38 (d, ^3J = 8.6 Hz, 4H, Ar), 6.69 (dd, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.9 Hz, 2H, −CH═), 5.80 (d, $^3J_{trans}$ = 17.5 Hz, 2H, ═CH_2), 5.33 (d, $^3J_{cis}$ = 10.9 Hz, 2H, ═CH_2), 5.28−5.18 (m, 2H, −O−CH<), 2.27−2.22 (m, 2H, cyclic CH_2), 1.85−1.74 (m, 2H, cyclic CH_2), 1.67−1.43 (m, 2H, cyclic CH_2). ^{13}C NMR (67.7 MHz, $CDCl_3$): δ (ppm) = 165.8 (C═O), 141.8 (Ar), 130.0 (Ar), 129.3 (Ar), 126.0 (Ar), 135.9 (−CH═), 116.4 (═CH_2), 74.2 (−O−CH<), 30.2 (cyclic CH_2), 23.5 (cyclic CH_2). IR (KBr): ν (cm^{-1}) = 1715 (C═O, st), 1608 (C═C, st). Anal. Calcd for $C_{24}H_{24}O_4$ (376.5): C 76.57; H 6.43. Found: C 76.55; H 6.58.

(1*S*,2*S*)-1,2-Cycloheptanediyl Bis(4-vinylbenzoate) (1c). The same procedure as that for **1a** was applied to (1*S*,2*S*)-1,2-cycloheptanediol (**c**) (1.0 g, 7.7 mmol), 4-vinylbenzoyl chloride (4.4 g, 26 mmol), and 45 mL of pyridine. The crude product was purified by column chromatography on silica gel with diethyl ether/hexane (volume ratio 1/4) to give **1c** as a white solid. Yield: 2.4 g (79%). $[\alpha]_{435} = +580°$, $[\alpha]_D = +238°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 7.92 (d, ^3J = 8.6 Hz, 4H, Ar), 7.38 (d, ^3J = 8.6 Hz, 4H, Ar), 6.70 (dd, $^3J_{trans}$ = 17.8 Hz, $^3J_{cis}$ = 10.9 Hz, 2H, −CH═), 5.80 (d, ^3J = 17.5 Hz, 2H, ═CH_2), 5.44−5.38 (m, 2H, −O−CH<), 5.33 (d, $^3J_{cis}$ = 10.9 Hz, 2H, ═CH_2), 2.07−1.60 (m, 10H, cyclic CH_2). ^{13}C NMR (67.7 MHz, $CDCl_3$): δ (ppm) = 165.6 (C═O), 141.8 (Ar), 129.9 (Ar), 129.4 (Ar), 126.0 (Ar), 136.0 (−CH═), 116.4 (═CH_2), 76.5 (−O−CH<), 30.4 (cyclic CH_2), 28.2 (cyclic CH_2), 22.8 (cyclic CH_2). IR (KBr): ν (cm^{-1}) = 1714 (C═O, st), 1607 (C═C, st). Anal. Calcd for $C_{25}H_{26}O_4$ (390.5): C 76.90; H 6.71. Found: C 76.73; H 6.83.

(1*S*,2*S*)-1,2-Cyclooctanediyl Bis(4-vinylbenzoate) (1d). The same procedure as that for **1a** was applied to (1*S*,2*S*)-1,2-cyclooctanediol (**d**) (2.0 g, 14 mmol), 4-vinylbenzoyl chloride (10 g, 60 mmol), and 100 mL of pyridine. The crude product was purified by column chromatography on silica gel with diethyl ether/hexane (volume ratio 1/4) to give **1d** as a white solid. Yield: 4.6 g (11 mmol, 81%). $[\alpha]_{435} = +553°$, $[\alpha]_D = +209°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) = 7.90 (d, ^3J = 8.3 Hz, 4H, Ar), 7.36 (d, ^3J = 8.6 Hz, 4H, Ar), 6.68 (dd, $^3J_{trans}$ = 17.5 Hz, $^3J_{cis}$ = 10.9 Hz, 2H, −CH═), 5.79 (d, $^3J_{trans}$ = 17.5 Hz, 2H, ═CH_2), 5.52−5.50 (m, 2H, −O−CH<), 5.33 (d, $^3J_{cis}$ = 10.9 Hz, 2H, ═CH_2), 2.01−1.54 (m, 12H, cyclic CH_2). ^{13}C NMR (67.7 MHz, $CDCl_3$): δ (ppm) = 165.8 (C═O), 141.8 (Ar), 129.8 (Ar), 129.3 (Ar), 126.0 (Ar), 136.0 (−CH═), 116.3 (═CH_2), 76.3 (−O−CH<), 29.2 (cyclic CH_2), 25.6 (cyclic CH_2), 24.2 (cyclic CH_2). IR (KBr): ν (cm^{-1}) = 1714 (C═O, st), 1608 (C═C, st). Anal. Calcd for $C_{26}H_{28}O_4$ (404.5): C 77.20; H 6.98. Found: C 77.38; H 7.09.

Cyclocopolymerization. The copolymerization of **1** with styrene was carried out using AIBN in dry toluene at 60 °C under nitrogen atmosphere. The typical procedure was as follows: **1a** (0.47 g, 1.3 mmol), styrene (0.53 g, 5.1 mmol), AIBN (65 mg), and dry toluene (65 mL) were placed into a flask. This solution was degassed and back-filled with nitrogen three times. Polymerization was initiated by heating to 60 °C in a water bath. After an appropriate time (11 h in this case), the polymerization mixture was cooled in an ice bath, and the mixture was concentrated. The concentrated mixture was poured into methanol (ca. 150 mL), and the precipitate was filtered. The obtained white powder was purified by reprecipitation with chloroform−methanol and dried in vacuo. Yield: 0.21 g (21%). $M_n = 5.1 \times 10^3$, $M_w/M_n = 2.28$. $[\alpha]_{435} = +315°$ (*c* 1.0, $CHCl_3$).

Synthesis of Poly[(methyl 4-vinylbenzoate)-*co*-styrene] (3). The removal of the chiral template from copolymer **2** was carried out using KOH in aqueous methanol, and then the hydrolyzed copolymer was esterified by treatment with diazomethane in benzene/ether. A typical procedure was as follows: The solution of copolymer **2a** (150 mg, $f_1 = 0.42$) in THF (5.8 mL) was placed into a Teflon bottle equipped with a reflux condenser. 25 wt % Methanolic KOH (50 equiv to the carboxyl group in **2a**) was added to the solution. The mixture was refluxed for 50 h along with periodic addition of a small portion of water. After neutralization by 2 N HCl with cooling in an ice bath, the mixture was transferred to a cellulose tube and dialyzed for 2 days with distilled water. The aqueous solution was freeze-dried to yield a white powder. The powder was added to a mixture of a diethyl ether solution (60 mL, ca. 0.5 mol·L^{-1}) of diazomethane (ca. 30 mmol) and benzene (60 mL). The polymer was dissolved with evolution of nitrogen gas. The mixture was left for 48 h at room temperature and the solvent was removed under reduced pressure. The residue was dissolved in 1.0 mL of chloroform and the solution was poured into 50 mL of methanol. The white precipitate was filtered and dried in vacuo. Yield: 76 mg (62%). $M_n = 3.0 \times 10^3$; $M_w/M_n = 1.98$. $[\alpha]_{435} = +0.5°$ (*c* 1.0, $CHCl_3$).

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MA000853B