# Chirality Induction in Cyclopolymerization. 3. Template Effect of Chiral Acyclic 1,3-Glycols on the Cyclocopolymerizations of (*S*)-1,3-Butanediyl and (2*S*,4*S*)-2,4-Pentanediyl Bis(4-vinylbenzoate)s with Styrene

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ABSTRACT: The copolymerizations of (*S*)-1,3-butanediyl and (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate)s (**1a** and **1b**) ($M_1$) with styrene ($M_2$) were carried out using AIBN in toluene at 60 °C. The obtained copolymers (**2**) consisted essentially of the cyclic repeating and styrene units, because the characteristic absorption due to the vinyl protons disappeared in the $^1$H-NMR spectra. The copolymerization reactivities of **1a** and **1b** were higher than that of styrene, resulting in the mole fraction of the $M_1$ unit in the copolymer **2** being higher than that of the $M_2$ unit for every monomer feed. The monomer reactivity ratio, which was calculated by the Kelen−Tüdös method, was $r_1 = 4.39$ and $r_2 = 0.20$ for **1a** and $r_1 = 3.81$ and $r_2 = 0.28$ for **1b**. The specific rotation ($[\alpha]_{435}$, *c* 1.0 in $CHCl_3$) changed from +283° to +182° for **2a** and from +434° to +319° for **2b**. After removing the chiral templates from **2a** and **2b**, poly[(methyl 4-vinylbenzoate)-*co*-styrene]s (**3a** and **3b**) were obtained. The specific rotation ($[\alpha]_{435}$, *c* 1.0 in $CHCl_3$) varied from −0.5° to −24.0° for **3a** and from −0.4° to −46.3° for **3b**, which indicated that the (2*S*,4*S*)-2,4-pentanediyl template approximately doubled in effect for the asymmetric induction by comparison with the (*S*)-1,3-butanediyl one. A split Cotton effect with a negative Cotton effect and a positive one was observed for the CD spectrum of **1** and the reversed one for **3**. According to the CD exciton chirality method, the clockwise twist of the two 4-vinylbenzoates of **1** transmitted their chirality to **3** in which two **4**-vinylbenzoyl groups twisted counterclockwise, i.e., an (*R*,*R*)-configuration of vicinal (methyl 4-vinylbenzoate) units in the main chain.

## Introduction

The cyclocopolymerization of a divinyl monomer containing a chiral template with a monovinyl comonomer is an ingenious method for producing an optically active polymer whose chirality is due to configurational asymmetry.[1] For most optically active polymers obtained by various asymmetric induction systems, however, it is difficult to determine the stereochemistry of the chiral center in the resulting polymers. On the other hand, the absolute configurations of chiral diols and diamines can be determined by the exciton chirality method[2] and the Bijvoet method using X-ray crystal analysis. Recently, we found that the cyclocopolymerization method coupled with the exciton chirality method is useful for elucidating the asymmetric induction. For the cyclocopolymerizations of bis(4-vinylbenzoate)s of 2,3-*O*-isopropylidene-L-threitol, methyl 4,6-*O*-isopropylidene-α-D-glucopyranoside, and 1,2:5,6-di-*O*-isopropylidene-D-mannitol with styrene, the absolute configuration of the resulting polymers was determined by the exciton chirality method.[3] In order to clarify the scope and limits of the asymmetric polymerization method, therefore, it is important to study the effect of the chiral template structure, such as the acyclic and cyclic templates, the distance between the two functional groups in the template, and the number of chiral centers in the template, on the efficiency of the asymmetric induction in the resulting polymers. The present study focuses on the number of chiral centers in the acyclic template using (*S*)-1,3-butanediol and (2*S*,4*S*)-2,4-pentanediol.

In this paper, we report the radical cyclocopolymerizations of (*S*)-1,3-butanediyl and (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate)s with styrene. The chiral templates in the cyclic copolymers are then eliminated, and the materials are treated with diazomethane to form poly[(methyl 4-vinylbenzoate)-*co* styrene]s as shown in Scheme 1. The asymmetric induction of the copolymers is confirmed by chiroptical measurements, and the process of the asymmetric transfer from the monomers to the polymers is discussed on the basis of the exciton chirality method.

## Experimental Section

**Measurements.** $^1$H and $^{13}$C NMR spectra were recorded using a JEOL EX-270 instrument. UV spectra were recorded on a JASCO 660 UV/vis spectrophotometer. The molecular weights of the polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Waters M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex KF-804L). The number-average molecular weight ($M_n$) was calculated using polystyrene calibration. Optical rotations were determined with a JASCO DIP-140 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.** The syntheses of (*S*)-1,3-butanediyl and (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate)s were reported in previ-

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**Scheme 1**

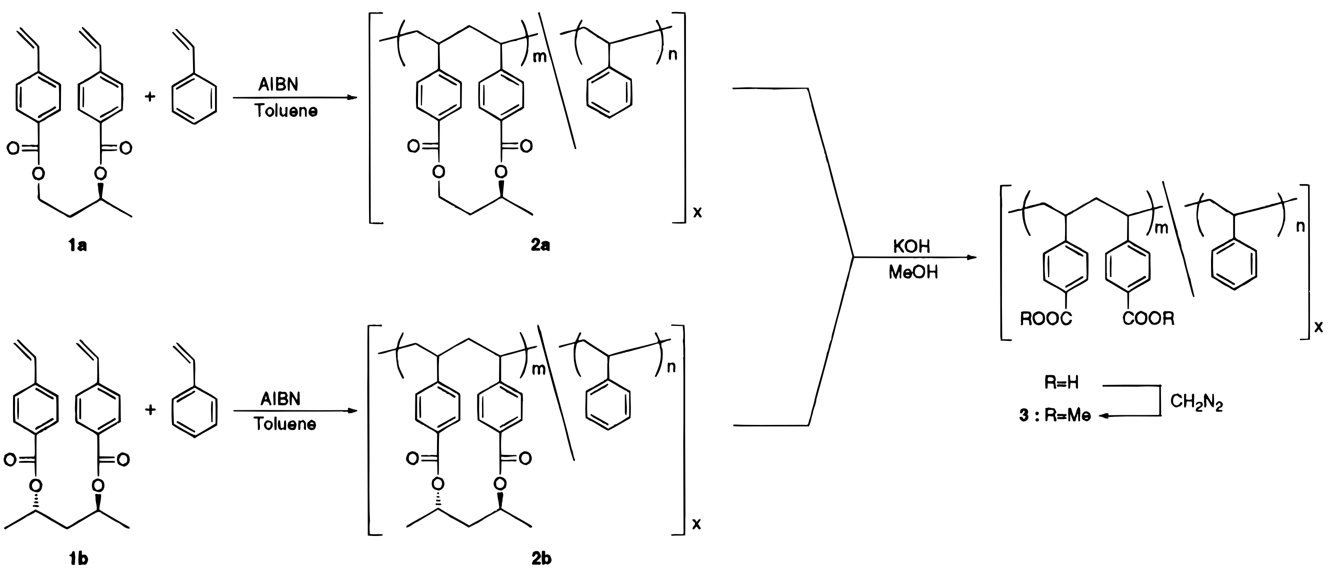


**Table 1. Cyclocopolymerizations of (*S*)-1,3-Butanediyl and (2*S*,4*S*)-2,4-Pentanediyl Bis(4-vinylbenzoate) (1a and 1b) ($M_1$) and Styrene ($M_2$) and Synthesis of Poly[(methyl-4-vinylbenzoate)-*co*-styrene] (3)**

| | copolymer **2**[a] | | | | | | copolymer **3**[b] | | |
|---|---|---|---|---|---|---|---|---|---|
| monomer | mole fraction of $M_1$ in monomer feed | time, h | yield, % | mole fraction of $M_1$ unit in copolymer[c] | $M_n$ ($M_w/M_n$)[d] | $[\alpha]_{435}$,[e] deg | yield, % | $M_n$ ($M_w/M_n$)[d] | $[\alpha]_{435}$,[e] deg |
| **1a** | 0.9 | 1.0 | 15 | 0.99 | 27800 (1.96) | +266 | 45 | 27100 (2.04) | −0.5 |
| | 0.8 | 1.5 | 15 | 0.96 | 15900 (2.95) | +261 | 55 | 21600 (1.97) | −2.2 |
| | 0.7 | 1.0 | 16 | 0.94 | 16400 (2.26) | +259 | 52 | 22900 (1.95) | −4.2 |
| | 0.6 | 2.0 | 26 | 0.87 | 13600 (2.04) | +283 | 53 | 14000 (1.79) | −6.9 |
| | 0.5 | 2.0 | 21 | 0.81 | 13200 (2.09) | +263 | 57 | 15600 (1.82) | −10.3 |
| | 0.4 | 3.0 | 24 | 0.76 | 9400 (1.85) | +252 | 60 | 10500 (1.79) | −13.3 |
| | 0.3 | 3.0 | 18 | 0.64 | 8700 (2.24) | +238 | 60 | 9800 (2.19) | −17.0 |
| | 0.2 | 4.0 | 16 | 0.53 | 4800 (2.38) | +227 | 45 | 6500 (1.57) | −24.0 |
| | 0.1 | 6.0 | 12 | 0.35 | 4300 (1.34) | +182 | 68 | 3900 (1.35) | −24.0 |
| **1b** | 0.9 | 1.0 | 22 | 0.97 | 37000 (1.73) | +434 | 32 | 28800 (1.92) | −0.4 |
| | 0.8 | 1.5 | 24 | 0.95 | 29300 (1.89) | +423 | 44 | 26800 (1.87) | −5.2 |
| | 0.7 | 1.8 | 24 | 0.89 | 31300 (1.89) | +394 | 41 | 21800 (1.98) | −9.4 |
| | 0.6 | 1.8 | 23 | 0.86 | 18300 (1.72) | +405 | 41 | 17600 (1.76) | −16.3 |
| | 0.5 | 2.5 | 22 | 0.79 | 20900 (2.25) | +385 | 72 | 15700 (2.12) | −19.7 |
| | 0.4 | 2.3 | 22 | 0.71 | 11200 (1.76) | +395 | 67 | 10700 (1.71) | −31.6 |
| | 0.3 | 4.0 | 21 | 0.61 | 9000 (2.09) | +354 | 64 | 6900 (2.16) | −36.4 |
| | 0.2 | 5.0 | 22 | 0.49 | 5000 (1.60) | +319 | 70 | 5500 (1.47) | −46.3 |

[a] Solvent, toluene; initiator, AIBN; temperature 60 °C; [**1** + St] = 0.1 mol·L$^{-1}$; [AIBN] = 6 mmol·L$^{-1}$. [b] Prepared from copolymer **2** through hydrolysis using KOH in aqueous MeOH for 50 h under reflux and then treatment with diazomethane in benzene−ether. [c] Determined by $^1$H and $^{13}$C NMR spectra. [d] Determined by GPC using a polystyrene standard. [e] Measured in $CHCl_3$ at 23 °C (*c* = 1.0).

ous papers.[4,5] Toluene and benzene were refluxed over sodium benzophenone ketyl and distilled just before use. α,α′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. HFIP was donated by Central Glass Co. and used without further purification.

**Cyclocopolymerization.** The copolymerization of **1** and 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 white powder was purified by reprecipitation with chloroform−methanol and dried *in vacuo*. The composition of **2** was determined from the area ratio of aromatic and aliphatic regions in the $^1$H NMR spectrum.

**Poly[(methyl 4-vinylbenzoate)-*co*-styrene] (3).** The removal of the chiral template from **2** was carried out using KOH in aqueous MeOH, and then the hydrolyzed copolymers were treated with diazomethane[6] in benzene/ether. The procedures were reported in previous papers.[3−5]

**Calculation of Molecular Mechanics.** The calculations were carried out using the standard MNDO-PM3 Hamiltonian, as implemented in the MOPAC (version 6.0) programs. The geometries of templates were fixed on each conformer as the other geometrical variables were optimized using the Eigenvector Following algorithm.

## Results and Discussion

**Cyclocopolymerization.** The copolymerizations of (*S*)-1,3-butanediyl and (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate)s (**1a** and **1b**) ($M_1$) with styrene ($M_2$) were carried out using AIBN in toluene at 60 °C, and the results are listed in Table 1. The polymerization systems were homogeneous, and the resulting copolymers (**2**) were soluble in chloroform and tetrahydrofuran. The number-average molecular weights ($M_n$s) of the polymers decreased with an increase in styrene (St) in the monomer feed and varied from 27 800 to 4300 for **2a** and from 37 000 to 5000 for **2b**. Figure 1a−d shows the $^{13}$C NMR spectra of monomers **1a** and **1b** and polymers **2a** and **2b**. The characteristic absorption at 136 and 116 ppm due to the vinyl protons disappeared for both copolymers so that **2a** and **2b** consisted essentially of the cyclic repeating and styrene units, i.e., the extent of cyclization for **1a** and **1b** was 100%. Such a high cyclization tendency, which is unusual because of the large ring size and steric repulsion, should be caused by the diluted polymerization condition ([**1** +

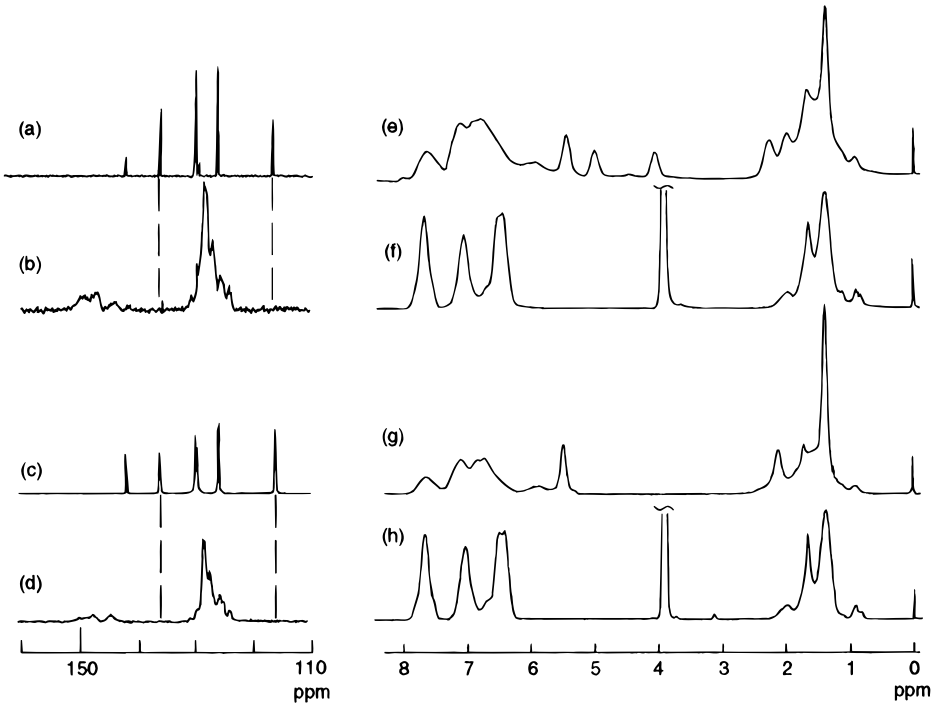


**Figure 1.** Expanded $^{13}C$ NMR spectra of monomers **1a** (a) and **1b** (b) and copolymers **2a** ($m/n$ = 0.53/0.47 in copolymer) (c) and **2b** ($m/n$ = 0.49/0.51 in copolymer) (d), and $^1H$ NMR spectra of copolymers **2a** (e), **3a** (f), **2b** (g), and **3b** (h) measured in $CDCl_3$ at 24 °C.

styrene] = 1.0). The copolymerization reactivities of **1a** and **1b** were higher than that of styrene, resulting in the mole fraction of the $M_1$ unit in copolymer **2** being higher than that of the $M_2$ unit for every monomer feed. For the cyclocopolymerizations of **1a** and **1b** with styrene, there were slight differences in the copolymerization reactivity, i.e., the monomer reactivity ratio was $r_1 = 4.39$ and $r_2 = 0.20$ for **1a** and $r_1 = 3.81$ and $r_2 = 0.28$ for **1b**. The specific rotation ($[\alpha]^{23}{}_{435}$, $c$ 1.0, $CHCl_3$) of **2a** and **2b** was almost constant at +260° and +400° above $f_1$ of 0.7, in spite of variations in the mole fraction of the chiral divinyl units. This chiroptical property suggests a new occurrence of chirality except for the template, i.e., the chirality induction in the polymer main chain.

**Template-Free Copolymers.** The asymmetric induction in the cyclocopolymerization systems should be confirmed by quantitatively removing the chiral templates from the cyclocopolymers. The removal of the chiral template from **2** was carried out using KOH in aqueous MeOH. The hydrolyzed copolymers were then treated with diazomethane. Figures 1f,h show the $^1H$-NMR spectra of the methylated polymers derived from **2a** and **2b**. The peaks at 3.6−5.2 ppm due to the ($S$)-1,3-butanediyl units and the peak at 5.3−5.4 ppm due to the (2$S$,4$S$)-2,4-pentanediyl units disappeared so that the lack of chiral templates was confirmed for both polymers. Therefore, the template-free polymers were poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**). Table 1 lists the results of the synthesis of **3**.

**Chiroptical Properties.** The specific rotation ($[\alpha]_{435}$, $c$ 1.0 in $CHCl_3$) changed from +283° to +182° for cyclopolymer **2a** and from +434° to +319° for cyclopolymer **2b**. After the chiral templates were removed, the obtained copolymers, i.e., poly[(methyl 4-vinylbenzoate)-*co*-styrene]s (**3a** and **3b**), showed optical activity as listed in Table 1. The specific rotation ($[\alpha]_{435}$, $c$ 1.0 in $CHCl_3$) increased with an increase in St in the monomer feed and varied from −0.5° to −24.0° for **3a** and from −0.4° to −46.3° for **3b**. The sign of these values is opposite to that for **2** at every composition. This result indicated that a new chirality was induced in the main chain of the monomeric units of **1** by the twist of ($S$)-1,3-butanediol and (2$S$,4$S$)-2,4-pentanediol templates.

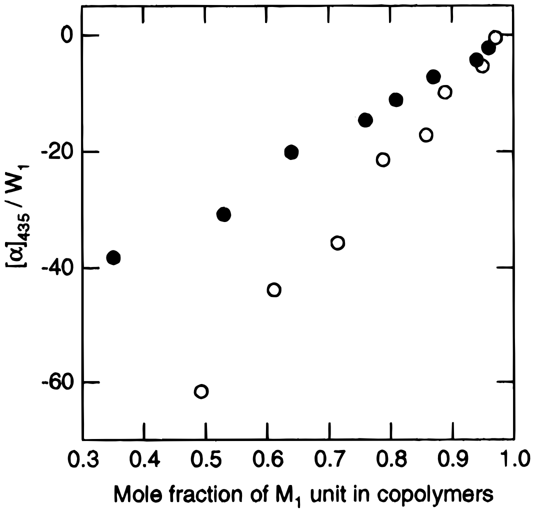


**Figure 2.** Specific rotations of copolymer **3a** (●) and **3b** (○) divided by weight fraction of $M_1$ unit in copolymer.

The rotatory power of each dibenzoate diad derived by hydrolysis of the $M_1$ unit was estimated from the ratio of the specific rotations of **3** to the weight fraction ($W_1$) of diad ($[\alpha]/W_1$). Figure 2 shows the ($[\alpha]/W_1$) as a function of the mole fraction of the diad in **3**. The values of specific rotation change from −0.5° to −38° for **3a** and from −0.4° to −62° for **3b**. Compared with **3a** having a similar composition in $[\alpha]/W_1$ value, **3b** had twice the value. For both **3a** and **3b**, the specific rotation increased with an increase in $M_2$ units in the copolymer composition. This result means that asymmetric inductivity increases with the decreasing se-

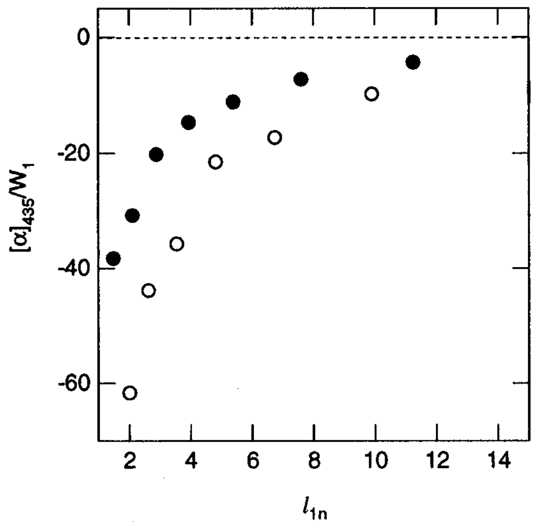


**Figure 3.** Specific rotations of copolymer **3a** (●) and **3b** (○) divided by the weight fraction of $M_1$ unit in copolymer **2a** and **2b** versus the number-average length of monomer **1a** and **1b** ($\bar{l}_{1n}$) in copolymer **2a** and **2b** calculated by eq 1.

quence of $M_1$ units. The isolation tendency of the diad can be estimated by the number-average length of $M_1$ runs ($\bar{l}_{1n}$),[7] which is calculated from the copolymerization parameter, $r_1$, by eq 1:

$$\bar{l}_{1n} = 1 + r_1\frac{f_1}{1-f_1} \qquad (1)$$

Figure 3 shows the $[\alpha]/W_1$ in **3** as a function of $\bar{l}_{1n}$. The $[\alpha]/W_1$ remarkably increases when the $\bar{l}_{1n}$ value is close to 1.0. This proves that the isolated dibenzoate diad clearly becomes a source for the appearance of chirality in **3**. Wulff proposed the mechanism of asymmetric induction such that the comonomer (A) adds to the cyclized divinyl unit (B—B) to form the optically active triad B—B—A.[1e] The chirality, therefore, is considered to be caused by a dibenzoate diad isolated by the comonomeric unit.

Figure 4 shows the CD and UV spectra of **1a** and **1b** in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). For the CD spectrum of **1a**, a positive Cotton effect at 282.7 nm ($\Delta\epsilon = +16.3$) and a negative one at 259.1 nm ($\Delta\epsilon = -7.5$) are exhibited in the region of $\pi \rightarrow \pi^*$ transition ($\lambda_{\max}$ 269.6 nm). The CD spectrum of **1b** is similar to that of **1a** which exhibits a positive Cotton effect at 282.6 nm ($\Delta\epsilon = +28.6$) and a negative one at 259.2 nm ($\Delta\epsilon = -14.7$) in the region of $\pi \rightarrow \pi^*$ transition ($\lambda_{\max}$ 270.5 nm). For the exciton coupling of two chromophores, the maximum wavelength ($\lambda_{\max}$) of the UV spectrum depends on the dihedral angle between the two benzoate groups. The value of $\lambda_{\max}$ for **1a** is 269.6 nm, which is very close to that of 270.5 nm for **1b**. This means that the dihedral angle between the two 4-vinylbenzoate groups for **1a** is same as that for **1b**. In addition, applying the exciton chirality method, both monomers **1a** and **1b** have a positive chirality and their benzoate chromophores, the two 4-vinylbenzoate groups, twist clockwise. Nakanishi et al. reported that the *A* value, the CD amplitude of exciton Cotton effects, is inversely proportional to the square of the distance between two chromophores.[2] The *A* value is +23.8 for **1a**, which is half of the value of +43.3 for **1b**. Therefore, the distance between the two 4-vinylbenzoates for **1a** is approximately 1.4 times that for **1b**.

Harada et al. reported that the exciton chirality method for determining the absolute stereochemistry on the basis of a chiral exciton coupling between two chromophores is effective for analyzing the stereochemistry of various chiral acyclic 1,3-glycol esters.[8] The difference in the CD spectrum between **1a** and **1b** is also estimated by calculating the most stable rotational conformation and its energy level. Because the monomers are free rotatomers at room temperature, the heat of formation of each rotamer for **1a** and **1b** are calculated by the MOPAC (version 6.0) molecular orbital package utilizing the PM3 Hamiltonian. For **1a**, nine rotational conformers can exist (Figure 5). The most stable conformer is **VI**$_a$, but it has a negative chirality and unsuitable conformation for the intramolecular cyclization of **1**. The CD spectrum of **1a** showing positive chirality is thus caused by the second stable conformer **V**$_a$ which is most preferred among the nine rotational conformers for cyclization. On the other hand, the most stable conformer among the six rotational conformers of **1b** with a positive chirality is **IV**$_b$,

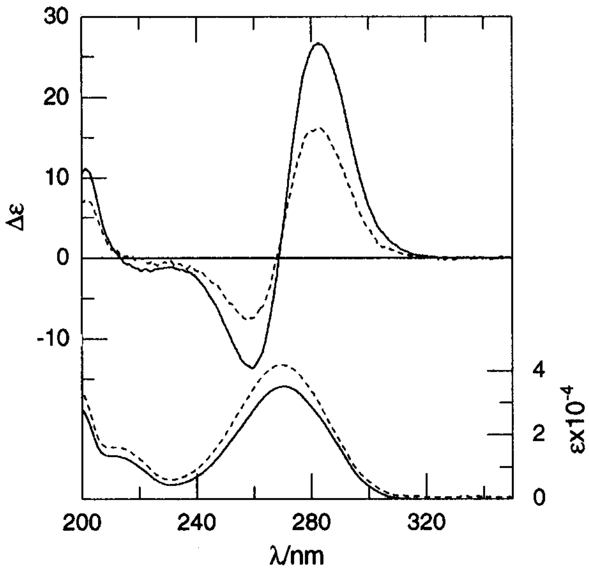


**Figure 4.** CD and UV spectra of monomer **1a** (- - -) and **1b** (—), measured in HFIP at 21 °C using a path length of 5 mm. Sample concentration was 0.117 mg/10 mL (3.33 × $10^{-5}$ mol·L$^{-1}$) (**1a**) and 0.206 mg/10 mL (5.65 × $10^{-5}$ mol·L$^{-1}$) (**1b**).

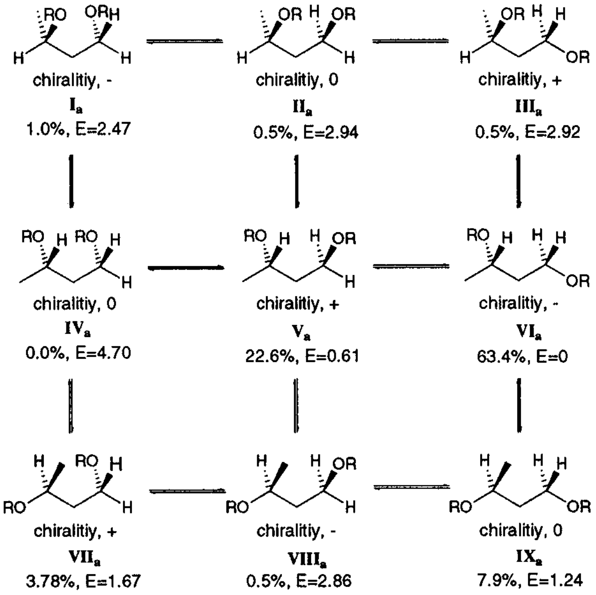


**Figure 5.** The rotational conformation, exciton chirality, and calculated steric energy and population at 25 °C of **1a**.

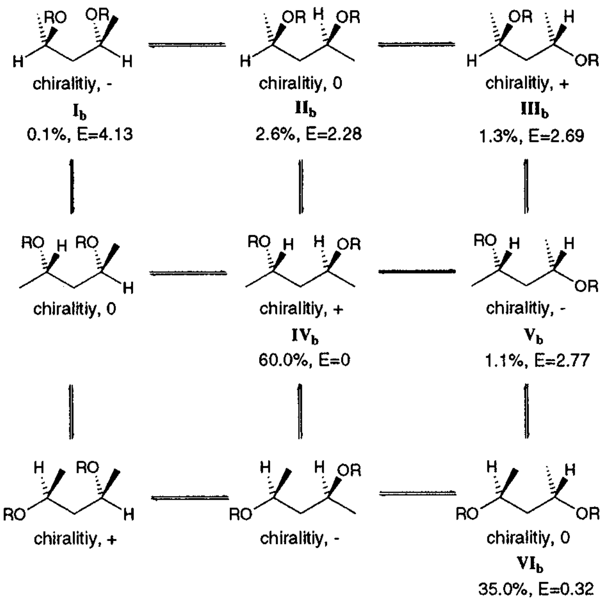


**Figure 6.** The rotational conformation, exciton chirality, and calculated steric energy and population at 25 °C of **1b**.

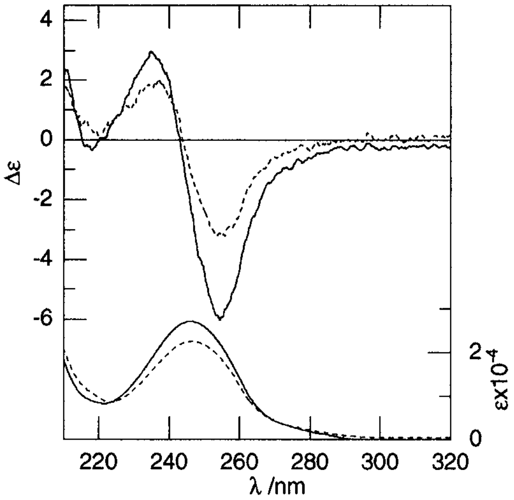


**Figure 7.** CD and UV spectra of copolymer **3a** ($m/n$ = 0.35/0.65 in copolymer) (- - -) and **3b** ($m/n$ = 0.49/0.51 in copolymer) (—), measured in HFIP at 21 °C. Sample concentration was 0.245 mg/10 mL (**3a**) and 0.277 mg/10 mL (**3b**). The $\Delta\epsilon$ and $\epsilon$ values were based on the concentration of methyl 4-vinylbenzoate units ($4.51 \times 10^{-5}$ mol·L$^{-1}$ (**3a**) and $6.40 \times 10^{-5}$ mol·L$^{-1}$ (**3b**)) calculated using the copolymer composition of 0.35 (**3a**) and 0.49 (**3b**). Path length was 5 mm.

the conformer which leads to the cyclization (Figure 6). The populations of conformers **VI**$_a$ and **V**$_b$ at 20 °C are calculated to be 22.6 and 60.0%, respectively, by the simple approximation of the Boltzmann distribution on the basis of the steric energy. This result should reflect in the differences in the CD spectra between **1a** and **1b**.

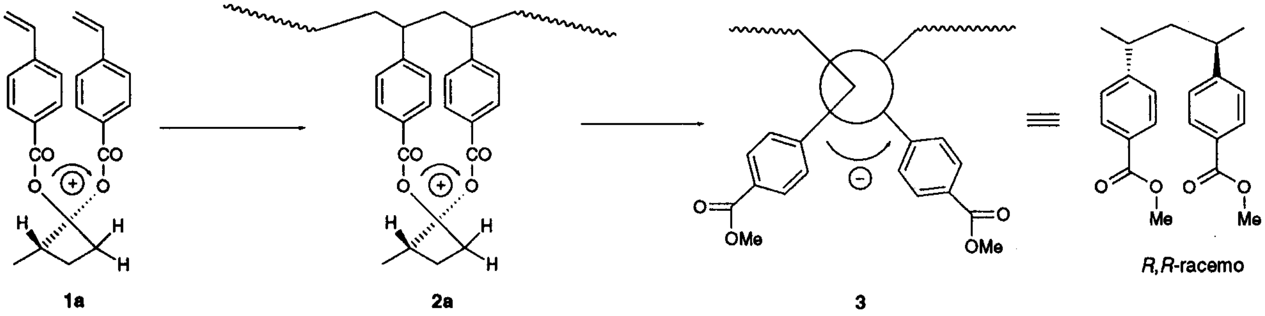
The chiroptical properties of **1a** and **1b** analyzed by the exciton chirality method and conformational calculations indicate that the chiral twist in **1b** is more efficient than that in **1a**. This causes the asymmetric induction in **3** from **1b** to be higher than that from **1a**. However, the steric effect for the transition state of intramolecular cyclization should be considered for the asymmetric induction. For the asymmetric induction based on the cyclocopolymerization method, many chiral templates have been examined, but the relation between the template structure and efficiency of asymmetric induction is obscure. In this study, we clearly found that the acyclic 1,3-glycol template with two chiral centers, (2*S*,4*S*)-2,4-pentanediol, almost doubles the asymmetric induction by comparison with (*S*)-1,3-butanediol having one center.

The CD and UV spectra of **3a** ($m/n$ = 0.35/0.65) and **3b** ($m/n$ = 0.49/0.51) in HFIP are shown in Figure 7. A split Cotton effect with a negative Cotton effect at 255.2 nm and a positive one at 237.2 nm is observed for the CD spectrum of **3a**. The CD spectrum of **3b** also shows a split Cotton effect with a negative Cotton effect at 254 nm and a positive one at 235 nm. These results indicate that both copolymers **3a** and **3b** have a negative chirality in which two 4-vinylbenzoyl groups are twisted counterclockwise, i.e., the configuration of the main chain carbon originating from the **1a** and **1b** units is an (*R*,*R*)-configuration. Scheme 2 represents the configurational change in the asymmetric inductive process. The chiral acyclic templates, (*S*)-1,3-butanediol and (2*S*,4*S*)-2,4-pentanediol, transmitted their chiralities to the main chain during the intramolecular cyclization to form an enantiomeric *R*,*R*-racemo configuration in the resulting polymer.

## Conclusions

Optically active poly[(methyl 4-vinylbenzoate)-*co*-styrene] was obtained through the radical cyclocopolymerizations of (*S*)-1,3-butanediyl and (2*S*,4*S*)-2,4-pentanediyl bis(4-vinylbenzoate)s (**1a** and **1b**) with styrene, followed by removing the templates. On the basis of the exciton chirality method, both monomers **1a** and **1b** have positive chirality and their benzoate chromophores, the two 4-vinylbenzoate groups, are twisted clockwise. On the other hand, copolymers **3a** and **3b** had negative chirality in which two 4-vinylbenzoyl groups are twisted counterclockwise, i.e., the configuration of the main chain carbon originating from the **1a** and **1b** units in an (*R*,*R*)-configuration. The efficiency of asymmetric induction in **3** from **1b** was higher than that from **1a**,

**Scheme 2. Schematic Conclusion of CD Spectrum Measurements for the Asymmetric Induction during Cyclocopolymerization of 1a and St**



which was caused by the fact that the chiral twist in **1b** was more efficient than that in **1a**.

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