Chirality Induction in Cyclopolymerization. 1. Cyclocopolymerization of 1,4-Bis[*O*-(4-vinylbenzoyl)]-2,3-*O*-isopropylidene-L-threitol with Styrene

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ABSTRACT: A bis(4-vinylbenzoate) monomer, 2,3-*O*-isopropylidene-1,4-bis[*O*-(4-vinylbenzoyl)]-L-threitol (**1**), was cyclocopolymerized with styrene. The resulting copolymers were hydrolyzed with KOH to remove the chiral template. Treatment with diazomethane then gave poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**5**). Polymer **5** showed a specific rotation, whose maximum value was +7.0° ($[\alpha]^{23}_{435}$, c = 1.0 in $CHCl_3$), and was optically active. The CD spectra of polymer **5** showed a splitting Cotton effect, i.e., a positive one at 255 nm and a negative one at 235 nm. Based on the exciton chirality method, polymer **5** possesses negative chirality. Consequently, it appeared that the stereochemistry of the carbon atom attached to the 4-benzoyl group is an *S* configuration.

Introduction

Much research has been done to obtain optically active vinyl polymers up to now.[1-3] Two types of the chiral vinyl polymers without any chirality in their side chain are currently known. The first type is a conformational chiral polymer that forms a one-handed helical structure, and the second consists of configurational polymers whose chirality is caused by the configuration of their asymmetric centers in their main chain. Our subject is the latter type. In order to obtain the configurationally chiral vinyl polymers, it is necessary to break down the symmetry of a stereoregular polymer chain. A cyclic[4-10] and an olefinic[11] structure in the polymer chain have been used as a component to destroy the symmetry.

The symmetry is also broken down by introducing comonomeric units. Wulff showed that the cyclocopolymerization of a divinyl monomer having a chiral template with achiral monovinyl monomers caused asymmetric induction to yield an optically active polymer with a main-chain chirality.[2] We also reported the cyclocopolymerization of 1,4-di-*O*-methacryloyl-2,3-*O*-isopropylidene-L-threitol with styrene,[12] from which the copolymer was optically active in spite of the removal of the chiral template. In these copolymerizations, the divinyl monomer forms a chiral threo diad and the monovinyl monomer separates the chiral diads from each other. The optical activity of these polymers is thus caused by the chiral diads. The absolute configuration of these diads is a most interesting subject. Wulff established the absolute configuration by comparing the chiroptical property of the copolymer with that of oligomeric model compounds.[13] No investigation, however, has been reported on the direct determination of the absolute configuration from characterization of the polymer structure.

The exciton chirality method (ECM)[14] is the most powerful method for determining the absolute configuration of chiral diols, diamines, etc., as well as the Bijvoet method using X-ray crystal analysis. The ECM is applicable to chiral dibenzoate compounds, and their absolute configurations are nonempirically determined from their exciton coupling in their circular dichroic (CD) spectra, which reflects a twist in the two longitudinal axes of the benzoate chromophores. The cyclocopolymerization of bis(4-vinylbenzoate) having a chiral template with a suitable monovinyl monomer should give a chiral dibenzoate diad, whose configuration can be determined by the ECM.

Here we report the cyclocopolymerization of 2,3-*O*-isopropylidene-1,4-bis[*O*-(4-vinylbenzoyl)]-L-threitol (**1**) with styrene (**2**) using a radical initiator (Scheme 1). In order to confirm the chiral induction in the polymer main chain, the resulting copolymers were hydrolyzed with potassium hydroxide and then treated with diazomethane to convert the poly(methyl 4-vinylbenzoate-*co*-styrene) (**5**). The homopolymer of **1** (**6**) and the copolymer of **1** and methyl 4-vinylbenzoate (**8**), polymer **9**, were also prepared and hydrolyzed to poly(methyl 4-vinylbenzoate) (**7**) to clarify the effect of the comonomer unit on the chirality of **5**. The chiroptical properties of monomer **1** and polymer **5** were measured, and the chirality induction and the absolute configuration in the polymer main chain are discussed on the basis of the ECM.

Results and Discussion

The copolymerizations of 2,3-isopropylidene-1,4-bis-[*O*-(4-vinylbenzoyl)]-L-threitol (**1**) with styrene (**2**) were carried out using 2,2′-azobis(2-methylpropionitrile) (AIBN) in toluene at 60 °C. The results are shown in Table 1. The entire polymerization system was homogeneous, and the resulting copolymers (**3**) were soluble in common organic solvents such as chloroform and tetrahydrofuran. The number-average molecular weight of these polymers ranged from 6700 to 23 500. Parts a and b of Figure 1 show the ^{1}H-NMR spectra of **1** and **3**, respectively. The characteristic absorptions due to the vinyl proton, which are observed at 5.3 and 5.8 ppm in

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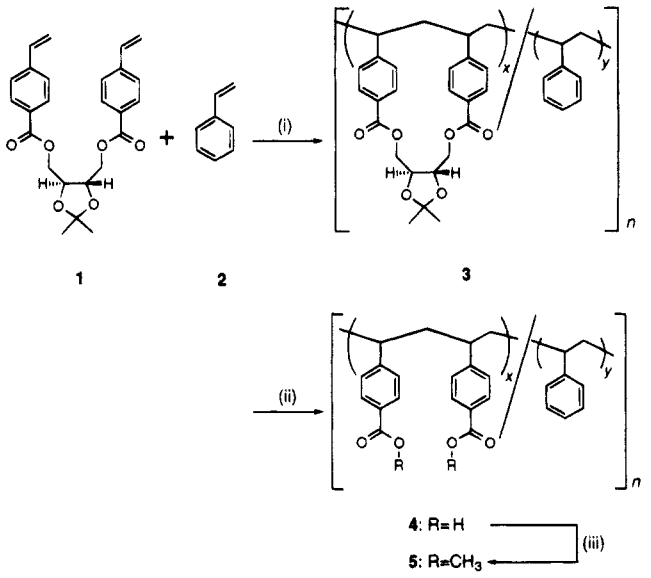
Scheme 1[a]



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

Table 1. Cyclocopolymerization of 2,3-*O*-Isopropylidene-1,4-bis[*O*-(4-vinylbenzoyl)]-L-threitol (1) with Styrene (2) Initiated by 2,2′-Azobis(2-methylpropionitrile) (AIBN)[a]

f_1[b]	time (h)	yield (%)	F_1[c]	M_n[d] × 10^{-3}	$[\alpha]^{23}_{435}$[e]
0.10	10	12	0.29	6.6	−27.2
0.20	6	14	0.44	6.7	−30.7
0.30	6	26	0.53	8.5	−33.3
0.40	3	16	0.60	11.0	−32.7
0.49	3	23	0.64	15.4	−31.6
0.56	2	19	0.69	17.0	−31.6
0.69	2	20	0.77	17.1	−32.4
0.78	1	21	0.83	23.5	−32.6

[a] All copolymerizations were carried out at 60 °C in toluene under a nitrogen atmosphere. The initial total monomer concentration ([1 + 2]) was 0.1 mol·L^{-1}, and the initiator concentration ([AIBN]) was 1.0 g·L^{-1}. [b] Mole fraction of **1** in the feed. [c] Mole fraction of the **1** unit in copolymer **3**, estimated from the ^{1}H-NMR spectrum. [d] Determined by GPC in THF using polystyrene as a standard. [e] Measured in $CHCl_3$, c = 1.0.

the spectrum of monomer **1**, disappeared in the spectrum of copolymer **3**. The vinyl groups in **1** were completely consumed as a result of the polymerization, thus producing the copolymers essentially consisting of cyclic repeating units. The copolymerization was terminated in the earlier step to determine the copolymerization parameters (r_1 and r_2) from the mole fractions of **1** in the feed (f_1) and copolymer **3** (F_1). The value F_1, which is listed in Table 1 and plotted versus f_1 in Figure 2, was determined from the area ratio of the aromatic and aliphatic regions in the ^{1}H-NMR spectrum. The Mayo−Lewis equation was fitted to the data, thus resulting in a reactivity ratio of $r_1 = 1.19$ and $r_2 = 0.17$.

The specific rotation ($[\alpha]^{23}_{435}$, c = 1.0, $CHCl_3$) of the copolymers was almost constant at −30° (Table 1), 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.

The chiral template was removed from copolymer **3** to confirm the chirality induction in the polymer main chain. Removal of the chiral template was carried out by alkali hydrolysis using potassium hydroxide. Subsequent treatment with diazomethane led to poly-

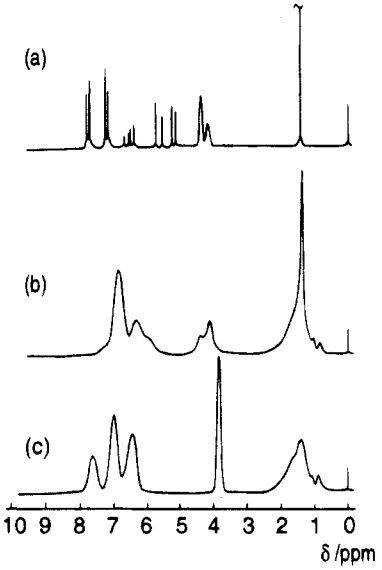


Figure 1. ^{1}H NMR spectra (270 MHz) of (a) monomer **1**, (b) polymer **3** (x/y = 0.27/0.73), and (c) polymer **5** (x/y = 0.27/0.73), measured in $CDCl_3$ using TMS as a reference.

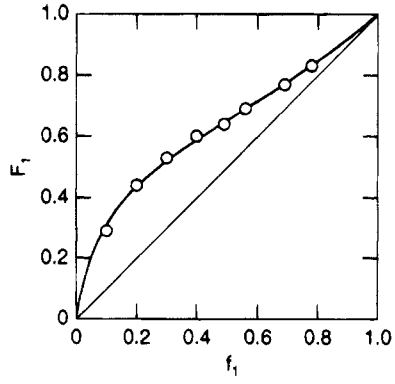


Figure 2. Mole fraction of **1** units in copolymer **3** (F_1) versus mole fraction of **1** in the feed (f_1). The circles are experimental results, and the solid line is the fit of the Mayo−Lewis equation to the data with $r_1 = 1.19$ and $r_2 = 0.17$. All copolymerization was carried out in toluene at 60 °C using AIBN as a initiator. The initial total monomer concentration was 0.1 mol·L^{-1}, and the initiator concentration was 1.0 g·L^{-1}.

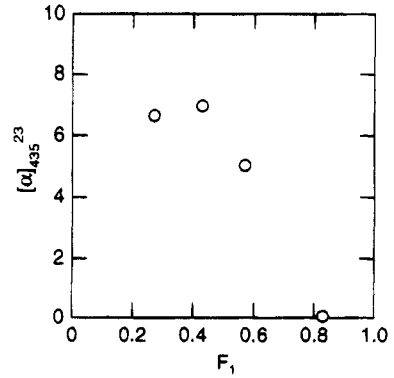


Figure 3. Specific Rotations ($[\alpha]^{23}_{435}$, c = 1.0 in $CHCl_3$) of polymer **5** versus mole fraction of **1** units in copolymer **3**.

(methyl 4-vinyl benzoate-*co*-styrene) (**5**). Parts b and c of Figure 1 show the ^{1}H-NMR spectra of **3** and **5**, respectively. No chiral template remained in polymer **5**, because an absorption at 3.6−5.2 ppm due to the template in Figure 1b entirely disappeared in Figure 1c.

Polymer **5** showed a rotatory power at every composition, thus showing optical activity. Figure 3 shows

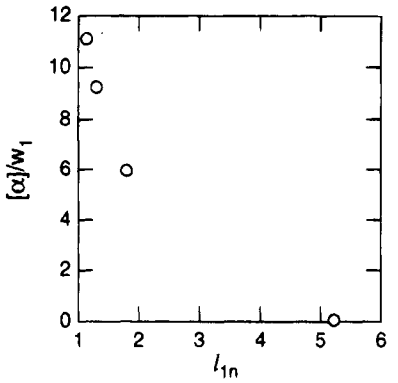


Figure 4. Specific rotations ($[\alpha]^{23}_{435}$, c = 1.0 in $CHCl_3$) of polymer **5** divided by the weight fraction of the **1** unit in polymer **3** (W_1) versus the number-average length of monomer **1** ($\bar{l}_{1n}$) in polymer **3** calculated by eq 1 with r_1 = 1.19.

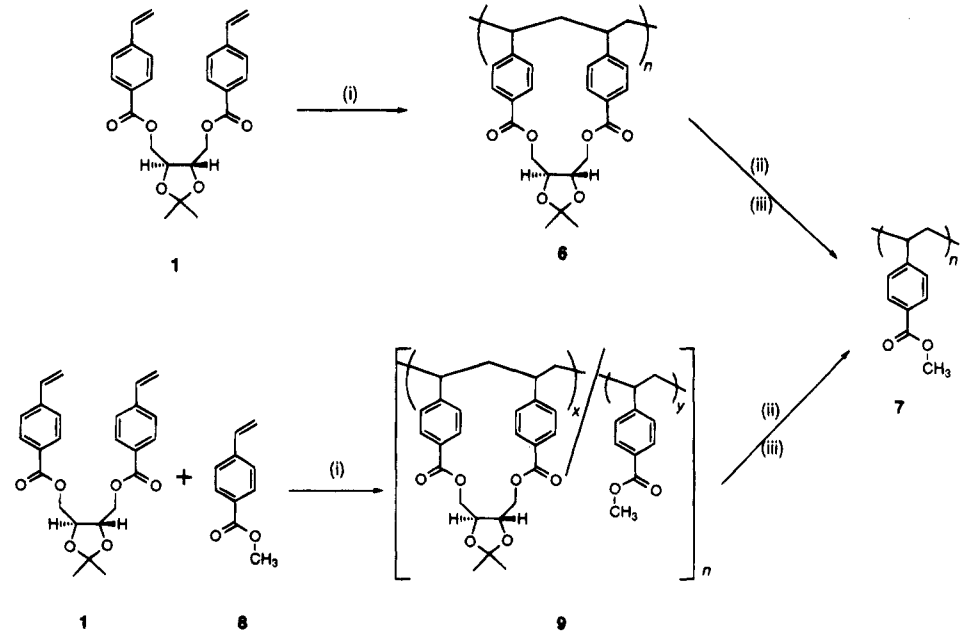
specific rotations ($[\alpha]^{23}_{435}$, c = 1.0, $CHCl_3$) of **5** as a function of F_1. The polymer had a maximum specific rotation of +7.0° at the F_1 value of 0.43. The chiroptical property confirms the chirality induction in the polymer main chain. Wulff proposed the mechanism of asymmetric induction such that the comonomer (B) adds to the cyclized divinyl unit (A–A) to form the optically active triad A–A–B.[13] The chirality, therefore, is considered to be caused by a dibenzoate diad isolated by the comonomeric unit. The number-average length of **1** runs ($\bar{l}_{1n}$),[16] which describes the isolation tendency of the diad, was 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 4 shows the specific rotations ($[\alpha]^{23}_{435}$, c = 1.9, $CHCl_3$) of **5** divided by its weight fraction of the **1** units in **5** (W_1) ($[\alpha]/W_1$), which means the average specific rotation of each dibenzoate diad as a function of $\bar{l}_{1n}$. $[\alpha]/W_1$ 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 **5**.

To prepare the optically active vinyl polymers through this asymmetric induction method using the divinyl monomer possessing the chiral template, the comonomeric units are not always necessary. Two types of synthetic routes to give optically active homopolymers have been reported: the homopolymerization[16] of a divinyl monomer with the chiral template and the copolymerization[17] of such a divinyl monomer with a monovinyl monomer which forms the same units as that derived from the divinyl monomer after removal of the template. In order to confirm the possibility of the formation of the chiral homopolymer from **1** and the effect of comonomeric units on the chirality of **5**, poly(methyl 4-vinylbenzoate) (**7**) was prepared through two different reaction pathways (Scheme 2). First, polymer **7** was obtained by the homopolymerization of **1** followed by hydrolysis and methylation. Second, methyl 4-vinylbenzoate (**8**) was copolymerized with **1**, and the resulting poly(**1**-*co*-**8**) was also changed to **7**. Polymer **7** from both methods contains the dibenzoate diad. The former does not possess a comonomeric unit to destroy the asymmetry of the main chain, while the latter has a comonomeric unit the same as the component of the diad. The soluble and gel-free **6** was obtained using the same conditions as that in Table 1. The specific rotation ($[\alpha]^{23}_{435}$, c = 1.0 in $CHCl_3$) was −30.5°. The ^1H- and ^{13}C-NMR spectra of **6** indicated no residual vinyl groups; hence, it essentially consisted of cyclic repeating units. A similar procedure for hydrolysis of **3** was adopted for **6** to give **7**, which did not show a significant specific rotation. The copolymerization of **1** and **8** was then carried out at an f_1 of 0.31. The resulting polymer **9**, with F_1 = 0.41, a M_n of 19 000, and an $[\alpha]^{23}_{435}$ of −19.1°, was obtained in 31% yield. The cyclization was completed as well as the cases of **3** and **6**. Polymer **7** from **9** was also not optically active. From both pathways, the optically active homopolymers, **7**, could not be obtained. Although we need information about the tacticity of polymer **7** explain this result, our attempts to determine the tacticity using NMR techniques have not succeeded. This point will be dealt with in a further study. The difference between the optically active

Scheme 2[a]



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

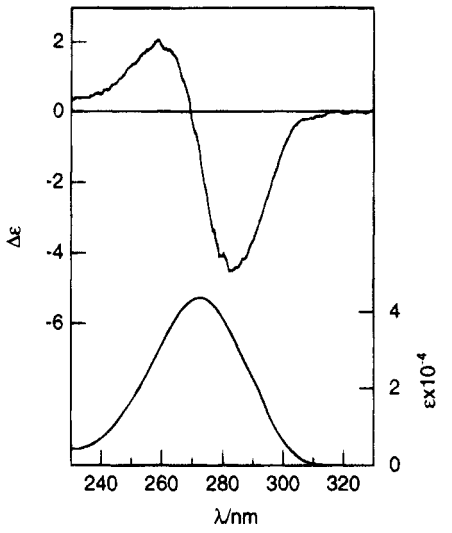
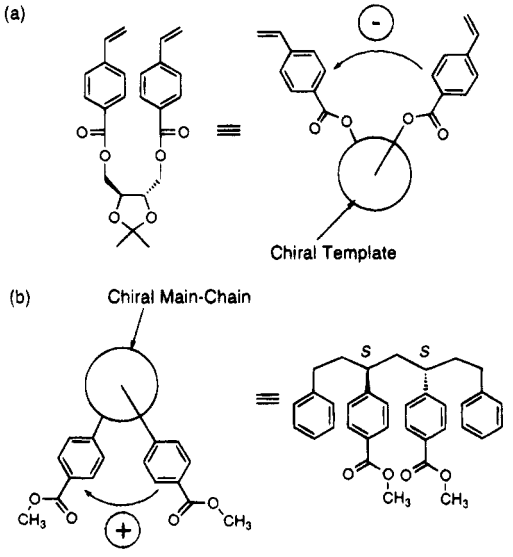


Figure 5. CD (upper) and UV (lower) spectra of monomer **1**, recorded in HFIP at 21 °C using a path length of 5 mm. Sample concentration was 30 mg·L^{-1} (0.071 mmol·L^{-1}).

Scheme 3



polymer **5** from **3** and the inactive **7** is the comonomeric unit, which significantly influences the occurrence of chirality induction. When the comonomer is different from the component of the chiral diad, the resulting copolymer becomes optically active. The comonomeric styrene units in **5** serve to break down the symmetry of the main chain.

The CD and UV spectra of **1** are shown in Figure 5. The CD spectrum exhibits a negative Cotton effect at 282 nm and a positive one at 258 nm, which is a typical splitting Cotton effect consistent with a UV absorption maximum at 272 nm. According to the ECM, monomer **1** has a negative chirality in which two 4-vinylbenzoyl groups are twisted counterclockwise (Scheme 3a) as expected from the template configuration. A CD spectrum of **3** (x/y = 0.27/0.73) (Figure 6) showed a more complex spectrum having three peaks, i.e., the two negative Cotton effects at 271 and 228 nm and a positive one at 249 nm, which could not be analyzed by the ECM; thus, further study is necessary.

The CD spectrum of **5** (x/y = 0.27/0.73) (Figure 7) also showed a splitting Cotton effect, with a positive Cotton effect at 255 nm and a negative one at 235 nm. Contrary to monomer **1**, copolymer **5** possesses a positive chirality in which two benzoyl groups are twisted clockwise (Scheme 3b). We should know the conformation of the main chain in solution to determine the absolute configuration of copolymer **3** using the ECM. Harada et al. reported that the dibenzoates of some linear alkanediols such as 2,4-pentane and 1,3-butanediols preferred an expanded zigzag conformation.[18-20] This might be a model for considering the application of the ECM to the polymer system. We assumed that copolymer **5** mainly takes a zigzag conformation when the CD spectra were recorded. Using this assumption, the configuration of the main-chain carbon that originated from the **1** units was determined to be an *S,S*-configuration, which was directly affected by the twist of the chiral template.

Scheme 4 presents the schematic conclusion of the CD spectral investigation. The L-threitol template having an *R,R*-configuration transmitted its chirality to the main chain during the intramolecular cyclization to form an enantiomeric *S,S*-racemo configuration in poly-

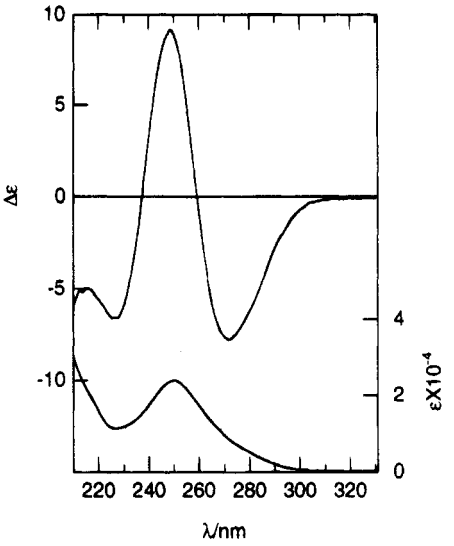


Figure 6. CD (upper) and UV (lower) spectra of polymer **3** (x/y = 0.27/0.73), recorded in HFIP at 21 °C using a path length of 5 mm. Sample concentration was 65 mg·L^{-1} (0.092 mmol·L^{-1} of the **1** unit). The $\Delta\epsilon$ values were estimated on the basis of the concentration of the **1** unit.

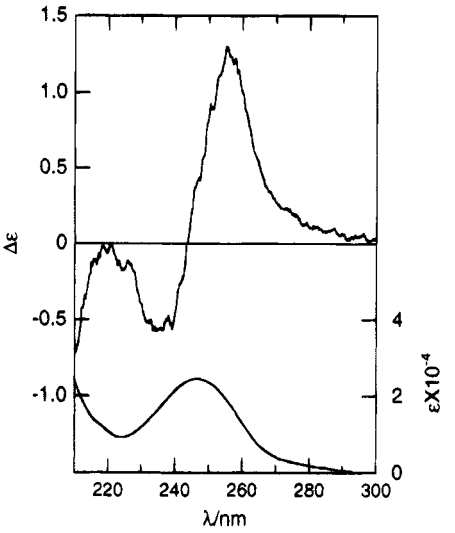
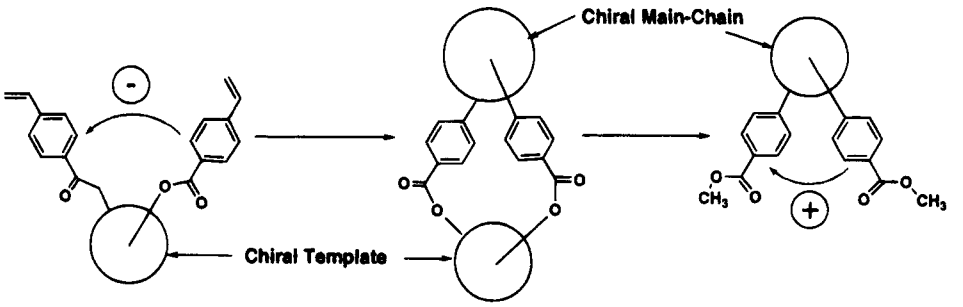


Figure 7. CD (upper) and UV (lower) spectra of polymer **5** (x/y = 0.27/0.73), recorded in HFIP at 21 °C using a path length of 5 mm. Sample concentration was 62 mg·L^{-1} (0.104 mmol·L^{-1} of the **1** unit). The $\Delta\epsilon$ values were estimated on the basis of the concentration of the **1** unit.

Scheme 4



mer **5**. The present investigation is the first example in which the ECM is adopted for determining the main-chain configuration of the chiral polymer. The ECM was used for determining the absolute configuration of the polymer during the cyclocopolymerization in which the chirality was induced by the chiral template. For stereochemistry, the ECM is a very powerful tool not only in organic chemistry but also in polymer chemistry.

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 weight of the resulting polymers was 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 on the basis of a polystyrene calibration. Optical rotations were determined with a Jasco DIP-140 digital polarimeter. CD spectra were measured at 21 °C in hexafluoroisopropyl alcohol (HFIP) with a 0.5-cm path length using a Jasco J-720 spectropolarimeter.

Materials. Toluene and benzene were distilled from sodium benzophenone ketyl. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol. Hexafluoroisopropyl alcohol was obtained from the Central Glass Co. and used without further purification.

2,4-Di-*O*-isopropylidene-1,4-bis[*O*-(4-vinylbenzoyl)]-L-threitol (1). A solution of 2,3-*O*-isopropylidene-L-threitol[19] (11 g, 0.069 mol) and triethylamine (28 g, 0.28 mol) in benzene (500 mL) was cooled to 5 °C in an ice bath. To this solution was gradually added a solution of 4-vinylbenzoyl chloride[20] (24 g, 0.15 mol) in benzene (150 mL) so that the temperature of the solution did not rise over 10 °C. The reaction mixture was stirred overnight at room temperature. The precipitate was filtered off, and the filtrate was successively washed with several portions of aqueous potassium bicarbonate and water and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, recrystallization from ether gave the final product as white crystals. Yield: 25 g (0.059 mol, 86%). MP: 89 °C. $[\alpha]^{23}_D = -19.7°$ ($c = 1.0$, $CHCl_3$). ^{1}H NMR (270 MHz, $CDCl_3$): δ 8.01 (d, ^3J = 8.3 Hz, 4H, Ar), 7.45 (d, ^3J = 8.3 Hz, 4H, Ar), 6.74 (dd, $^3J_{trans}$ = 17.8 Hz, $^3J_{cis}$ = 10.9 Hz, 2H, =CH−), 5.86 (d, $^3J_{trans}$ = 17.8 Hz, 2H, =CH_2), 5.39 (d, $^3J_{cis}$ = 10.9 Hz, 2H, =CH_2), 4.44−4.78 (m, 6H, CH_2 and CH), 1.47 (s, 6H, CH_3). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 165.9 (C=O), 142.2, 130.0, 128.6, 126.1 (arom), 135.9 (=CH−), 116.7 (CH_2=), 110.4 (C), 76.2 (CH), 64.2 (CH_2), 27.1 (CH_3). Anal. Calcd for $C_{25}H_{26}O_6$ (422.5): C, 71.06; H, 6.21. Found: C, 71.84; H, 6.38.

Polymerization. Copolymerizations were performed in a dried glass ampule under a N_2 atmosphere. The typical procedure was as follows: **1** (0.714 g, 1.83 mmol), styrene (0.286 g, 2.74 mmol), 2,2′-azobis(2-methylpropionitrile) (46 mg), and dry toluene (45.7 mL) were placed in a glass ampule. This solution was degassed *in vacuo*, and gaseous N_2 was introduced. Polymerization was initiated by heating to 60 °C in a water bath. After 3 h, the polymerization mixture was poured into methanol (500 mL) and the precipitate was filtered. The obtained white powder was purified by reprecipitation with chloroform−methanol and dried *in vacuo*. Yield 0.16 g (16%). The composition of **3** was 0.60/0.40 (x/y) which was estimated from the area ratio of aromatic and aliphatic regions in the ^{1}H-NMR spectrum.

Alkali hydrolysis of 3 to 4. A typical procedure was as follows. The solution of **3** (0.10 g, x/y = 0.60/0.40) in THF (4 mL) was place in a Teflon bottle equipped with a reflux condenser. To this, 25% methanolic KOH (50 equiv to the C=O group in **3**) was added. The reaction mixture was refluxed for 50 h along with periodic addition of a small portion of water. After neutralization by 2 N hydrochloric acid 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. This was used in the next step without further purification. Yield 62 mg (87%).

Methylation of 4 to 5. A typical procedure was as follows. To a mixture of an ether solution (60 mL, ca. 0.5 mol·L^{-1}) of diazomethane (ca. 30 mmol) and benzene (60 mL) was added a finely divided hydrolyzed copolymer (**4**; 62 mg, 0.88 mmol of the C=O group). The polymer was dissolved with evolution of nitrogen gas. The mixture was left alone for 14 h at room temperature, and all solvents were removed under reduced pressure. The residue was dissolved in 0.5 mL of chloroform and the solution was poured into 50 mL of methanol. The white precipitate was filtered and dried *in vacuo*. Yield: 61 mg (97%).

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