Chirality Induction in Cyclocopolymerization XI. Bulkiness Effect of 1,2-Diol Templates on Cyclocopolymerizations of Bis(4-vinylbenzoate)s with Styrene

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ABSTRACT: The radical cyclocopolymerizations of (*R*)-1-phenyl-1,2-ethanediyl, (*R,R*)-1,2-diphenyl-1,2-ethanediyl, and (*R,R*)-1,2-di(1-naphthyl)-1,2-ethanediyl bis(4-vinylbenzoate)s (**1d**, **1e**, and **1f**) with styrene yielded copolymer **2** with new chirality in the main chain. The chirality induction was based on the configurational arrangement. Optically active poly(methyl 4-vinylbenzoate-*co*-styrene) (**3**) was obtained by the removal of the chiral template in copolymer **2**, followed by the treatment with diazomethane. The template having (*R*)- and (*S*)-configuration transmitted its chirality to the main chain in the intramolecular cyclization of divinyl monomers to form the enantiomeric (*S,S*)- and (*R,R*)-racemo units, respectively. Repulsive steric interactions of the substituents restricted rotation around single bonds in the 1,2-diol templates to improve the selectivity between two racemo units.

KEY WORDS Chirality Induction / Divinyl Monomer / Radical Cyclocopolymerization / 1,2-Diol Template / Racemo-Configuration / Optically Active /

Asymmetric polymerization has recently developed as one of the most important methods for synthesizing optically active polymers. The cyclocopolymerization capable of forming monomer units without a plane of symmetry provides a useful means for the asymmetric polymerization. The origin of chirality on the basis of the stereogenic relationships in the main chain was theoretically deduced.¹ Regardless of the configuration in the B unit, when the diad sequence A-A has a racemo configuration, the triad sequence A-A-B becomes chiral in the copolymer. This phenomenon is synthetically realized by cyclocopolymerization, because the cleavage of the cyclic unit affords the diad sequence A-A. The A-A racemo diad units derived from the isolated cyclic units exhibit chirality when the comonomer units are present as spacers.

Wulff et al. synthetically realized the chirality induction during the cyclocopolymerization of the chiral bifunctional monomers, bis(4-vinylphenyl)boronate and bis[4-[(methacryloyl)oxy]phenyl]boronate carrying a 3,4-*O*-cyclohex-

ylidene-D-mannitol template, with achiral monomers.²⁻⁶ We have reported the cyclocopolymerizations of the bis(4-vinylbenzoate)s having the chiral template with styrene to yield optically active poly(methyl 4-vinylbenzoate-*co*-styrene)s^{7,8} (Scheme 1). The bis(4-vinylbenzoate) monomers (**1**) were useful for determining the absolute configuration of the cyclic units using the exciton chirality method. Copolymer **3** after the quantitative removal of the template became more active in chirality with increasing M₂ unit. The minimum chiral repeating unit is generated by the racemo diad of the M₁ unit separated by the M₂ units, namely, the isolated benzoate diad. Monomer **1** having the (*S*)-type template induced an enantiomeric (*R,R*)-racemo configuration in the main chain, and *vice versa*.

To clarify structural characteristics of the template for chirality induction, several types of templates, such as carbohydrates and synthetic chiral diols, were examined for the cyclocopolymerization of bis(4-vinylbenzoate)s with styrene.⁹⁻¹⁹ The

Scheme 1.

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cyclocopolymerizations of (2*S*,3*S*)-2,3-butanediyl, (2*S*,4*S*)-2,4-pentanediy, and (2*S*,5*S*)-2,5-hexanediy bis(4-vinylbenzoate)s (**1a**, **1b**, and **1c**) with styrene indicated that the extent of chirality induction increased with the templates in the order of **a** < **c** < **b**. The chirality induction of the monomers having these acyclic templates was characterized by means of a semiempirical MO calculation, which gave a result coinciding with the experimental ones.¹⁹

Optically active poly(methyl methacrylate-*co*-styrene)s were synthesized through the cyclocopolymerizations of 1,2:5,6-di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-L-threitol and D-mannitol with styrene.^{20,21} Although the former system suggested that the isolated M₁ unit participated in the occurrence of chirality, the latter system was distinct from the general case. The D-mannitol monomer had an outstanding characteristic in the significantly high fraction of tactic triad *rr* in the homopolymer and the larger probability of forming the racemo diad M₁M₁ in the copolymer. The origin of chirality, therefore, was assigned to the chiral tetrad MMA sequences.²¹ The occurrence behavior of chirality changed according to the template used. Since the 1,2-diol templates have a narrow distribution about the conformation and behave as a rigid template, they are suitable for examining the conformational effect of the monomers on the asymmetric cyclocopolymerization.

In this paper, the chirality induction during the cyclocopolymerization was studied for the bis(4-vinylbenzoate)s derived from three 1,2-diol templates, namely, (*R*)-1-phenyl-1,2-ethanediol (**d**), (*R,R*)-1,2-diphenyl-1,2-ethanediol (**e**), and (*R,R*)-1,2-di(1-naphthyl)-1,2-ethanediol (**f**). A difference of bulkiness in these templates elucidated the characteristics of chirality induction, in particular, the role of the conformers in the monomer as a result of rotation around single bonds in the 1,2-diol templates.

EXPERIMENTAL

(*R*)-1-Phenyl-1,2-ethanediyl Bis(4-vinylbenzoate) (**1d**)

The procedure is analogous to those reported in previous papers. To a solution of (*R*)-1-phenylethane-1,2-diol (5.0 g, 0.036 mol) in dry pyridine (200 mL) was gradually added 4-vinylbenzoyl chloride (21.1 g, 0.13 mol) at 5–10 °C, and the mixture was heated 40 °C with stirring for 4 hour. When the solution was stirred overnight at room temperature and diluted with ice-water, the resulting mixture was extracted with dichloromethane. After removal of the solvent under reduced pressure, the residue was purified by squat column chromatography on alumina with hexane/ether (volume ratio 4:1) to give 10.9 g of **1d** (yield 76 %) as a colorless crystal. $[\alpha]_D = -21.9^\circ$ and $[\alpha]_{435} = -74.5^\circ$ (c 1.0 in CHCl₃ at 24 °C). ¹H NMR (270 MHz, CDCl₃): δ = 8.06 (d, ³*J* = 8.6 Hz, 4H, ArH), 7.55–7.37 (m, 9H, ArH), 6.75 (dd, *J*_{trans} = 17.3 Hz, *J*_{cis} = 10.9 Hz, 1H, -CH=CH₂), 6.73 (dd, *J*_{trans} = 17.3 Hz, *J*_{cis} = 10.9 Hz, 1H, -CH=CH₂), 6.42 (dd, *J* = 4.0 Hz, *J* = 7.9 Hz, 1H, CH), 5.87 (d, *J*_{trans} = 17.5 Hz, 1H, -CH=CH₂), 5.85 (d, *J*_{trans} = 17.5 Hz, 1H, -CH=CH₂), 5.39 (d, *J*_{cis} = 10.9 Hz, 1H, -CH=CH₂), and 5.38 ppm (d, *J*_{trans} = 10.9 Hz, 1H, -CH=CH₂); ¹³C NMR (67.7 MHz, CDCl₃): δ = 165.9 and 165.5 (C=O), 142.2, 142.1, 136.6, 130.1, 129.0, 128.8, 128.7, 126.7, and 126.1 (ArC), 135.9 (-CH=CH₂), 116.7 and 116.6 (-CH=CH₂), 73.9 (CH), and 66.6 ppm (OCH₂). Anal. Calcd for C₂₆H₂₂O₄ (398.5): C, 78.36; H, 5.58. Found: C, 78.30; H, 5.71.

(*R,R*)-1,2-Diphenyl-1,2-ethanediyl Bis(4-vinylbenzoate) (**1e**)

The procedure is similar to that used for **1d**. By a series of reactions from (*R,R*)-1,2-diphenyl-1,2-ethanediol (7.8 g, 0.036 mol) and 4-benzoyl chloride (18.3 g, 0.11 mol) 11.5 g of **1e** (yield 66 %) was obtained as a colorless powder. $[\alpha]_D = +92.0^\circ$ and $[\alpha]_{435} = +179.4^\circ$ (c 1.0 in CHCl₃ at 24 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.00 (d, ³*J* = 8.5 Hz, 4H, ArH), 7.42 (d, ³*J* = 8.5 Hz, 4H, ArH), 7.23–7.22 (m, 10H, ArH), 6.72 (dd, *J*_{trans} = 17.6 Hz, *J*_{cis} = 11.0 Hz, 2H, -CH=CH₂), 6.43 (s, 2H, CH), 5.83 (dd, *J*_{trans} = 17.6 Hz, *J*_{gem} = 0.7 Hz, 2H, -CH=CH₂), and 5.36 ppm (dd, *J*_{cis} = 11.0 Hz, *J*_{gem} = 0.5 Hz, 2H, -CH=CH₂). ¹³C NMR (100 MHz, CDCl₃): δ = 165.3 (C=O), 142.1, 136.0, 130.0, 129.0, 128.5, 128.3, 127.6, and 126.1 (ArC), 136.1 (-CH=CH₂), 116.6 (-CH=CH₂), and 77.8 ppm (CH). Anal. Calcd for C₃₂H₂₆O₄ (474.6): C, 80.99; H, 5.52. Found: C, 80.84; H, 5.65.

(*R,R*)-1,2-Di(1-naphthyl)-1,2-ethanediyl Bis(4-vinylbenzoate) (**1f**)

The procedure is similar to that used for **1d**. Reaction of (*R,R*)-1,2-di(1-naphthyl)-1,2-ethanediol (7.5 g, 0.024 mol) with 4-vinylbenzoyl chloride (12.0 g, 0.073 mol) gave 11.5 g of **1f** as a colorless crystal. $[\alpha]_D = +207.5^\circ$ and $[\alpha]_{435} = +479.0^\circ$ (c 1.0 in CHCl₃ at 24 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.31 (br, 2H, CH), 8.02 (d, ³*J* = 8.5 Hz, 4H, ArH), 7.72–7.20 (m, 18H, ArH), 6.71 (dd, *J*_{trans} = 17.6 Hz, *J*_{cis} = 11.0 Hz, 2H, -CH=CH₂), 5.83 (d, *J*_{trans} = 17.6 Hz, 2H, -CH=CH₂), and 5.36 ppm (d, *J*_{cis} = 11.0 Hz, 2H, -CH=CH₂). ¹³C NMR (100 MHz, CDCl₃): δ = 165.6 (C=O), 142.1, 133.7, 132.1, 131.0, 130.1, 129.3, 129.0, 128.7, 126.7, 126.3, 126.2, 125.5, 124.8, and 123.5 (ArC), 136.0 (-CH=CH₂), 116.6 (-CH=CH₂), and 77.3 ppm (CH). Anal. Calcd for C₄₀H₃₀O (574.7): C, 83.60; H, 5.26. Found: C, 83.90; H, 5.47.

Cyclocopolymerization

The cyclocopolymerization of **1** with styrene was carried out using AIBN in toluene at 60 °C. The total concentration of both monomers was 0.1 mol·L⁻¹ in the copolymerizations. 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 vacuum.

Poly(methyl 4-vinylbenzoate-*co*-styrene) (**3**)

The removal of the chiral template from **2** was carried out using methanolic KOH. After neutralization with hydrochloric acid, the solution was dialyzed using a cellophane tube and later concentrated by freeze-drying. The hydrolyzed copolymers were treated with diazomethane in benzene/ether, whereupon copolymers **3** were obtained.

RESULTS AND DISCUSSION

Cyclocopolymerization

Table I lists the results of the copolymerizations of **1d**, **1e**, and **1f** (M₁) with styrene (M₂) which were carried out using AIBN in toluene at 60 °C. The polymerizations homogeneously proceeded and the resulting copolymers (**2d**, **2e**, and **2f**) were soluble in chloroform and tetrahydrofuran. Copolymers **2d**, **2e**, and **2f** contained a small amount of residual double bonds which was shown by the presence of the characteristic absorptions due to the vinyl groups in their ¹H and ¹³C NMR spectra. The extent of cyclization (*f*_c) was estimated from the area ratio between the vinyl and aliphatic regions in the ¹H NMR spectra of **2d** and **2e** and from that between the peaks of the carbonyl

and vinyl carbons in the inverse gated coupling ^{13}C NMR of **2f**. The f_c values ranged from 0.62 to 0.89 for **2d** and from 0.85 to 0.95 for **2e**, and those for **2f** went up to over 0.99. The monomer reactivity ratios were $r_1=3.08$ and $r_2=0.30$ for **1d** which were determined on the basis of the Roovers–Smets expression with consideration of the extent of cyclization^{21,22} and $r_1=3.67$ and $r_2=0.81$ for **1e** which were derived using the Mayo–Lewis equation without consideration for cyclization.

The chirality induction in the cyclocopolymerization was confirmed by the quantitative removal of the chiral templates from copolymer **2**. Copolymer **3** exhibited the expected optical activity due to the main chain chirality. The optical activities of copolymer **3** increased with a decrease in the M_1 fraction in the copolymer and the specific rotations ($[\alpha]_{435}^{24}$, c 1.0 in CHCl_3) changed from 0 to $+4^\circ$ for **3d**, from $+2$ to $+18^\circ$ for **3e**, and from $+9$ to 21° for **3f**. The CD spectra of monomers **1d** and **1e** showed the split Cotton effect with a negative first and a positive second Cotton effect (Figure 1). According to the exciton chirality method, these CD spectra indicate that the two benzoate chromophores in the monomer twist counterclockwise. This method could not be applied to the CD spectrum of **1f** without the split Cotton effect. The CD spectra of copolymers **3d**, **3e**, and **3f** showed the split Cotton effect with a positive first and a negative second Cotton effect, thus indicating that the two methyl benzoate chromophores in the copolymer twist clockwise. A segmental distribution with a high content of (*S,S*)-racemo benzoate diads was favored in copolymers **3d**, **3e**, and **3f**. Templates **d**, **e**, and **f** having (*R*)-configuration induced the chirality of the (*S,S*)-racemo configuration in the main chain.

Template Effect

On the first-order Markov model and perfect cyclization, the weight fraction of the isolated benzoate diad ($P(1, M_1)$) could be calculated as follows:²³

Figure 1. CD and UV spectra of (a) monomers **1d-f**, and (b) copolymers **3d-f**.

$$P(1, M_1) = W_1 \times \left(\frac{[M_2]}{r_1[M_1] + [M_2]} \right)^2 \quad (1)$$

where W_1 is the weight fraction of the M_1 unit and r_1 is the monomer reactivity ratio of monomer **1**. Figure 2 shows the plots of the specific rotations of copolymers **3d** and **3e** versus the weight fraction of the isolated M_1 unit, $P(1, M_1)$, along with the related data^{17,18} of copolymers **3a** and **3h**. Each of the copolymers showed a good linearity of the plots. This result means that the source of chirality in copolymer **3** is attributed to the isolated benzoate diad. The extent of chirality induction increased in the order of **d** < **a** < **e** = **h**. Template **d** with one phenyl group is less efficient than template **a** with two methyl groups, but more efficient than (*S*)-1,2-propanediyl template^{13,14} with one methyl group. Template **e** with two phenyl groups is more efficient than template **a** and is comparable to template **h**^{13,18} with two dioxolane rings. Bulkiness of the substituents at the 1,2-positions of the 1,2-diol templates plays an important role in the extent of chirality.

As described above, carbohydrate, namely, D-glucitol, D-mannitol, and D-iditol are the useful sources as templates. Monomers **1g**, **1h**, and **1i**, which were derived from 1,2:5,6-di-*O*-

Table I. Cyclocopolymerizations of Bis(4-vinylbenzoate)s (**1d-f**) (M_1) with Styrene (M_2) and Synthesis of Poly(methyl 4-vinylbenzoate-co-styrene)s (**3d-f**)^a

M_1	f_1^b	time, h	yield, %	copolymer 2					copolymer 3		
				F_1^c	f_c^d	M_n^e	M_w / M_n^e	$[\alpha]_{435}^{24, f}$, deg	M_n^e	M_w / M_n^e	$[\alpha]_{435}^{24, f}$, deg
1d	0.10	14.0	5	0.25	0.89	5700	1.91	-109	7800	1.90	+4
	0.20	11.0	9	0.39	0.86	10500	1.60	-143	7000	1.43	+3
	0.30	7.5	4	0.41	0.83	11000	1.95	-127	8200	1.47	+1
	0.40	9.0	17	0.58	0.86	14600	2.89	-99	13100	1.50	+1
	0.50	6.0	12	0.65	0.86	10500	3.38	-98	10300	1.55	0
	0.60	5.0	10	0.66	0.87	27300	2.65	-99			
	0.70	4.0	11	0.73	0.84	26200	4.27	-88			
	0.80	3.5	8	0.78	0.75	24800	4.13	-88			
	0.90	2.0	23	0.86	0.62	45900	3.33	-88			
1e	0.10	10.0	20	0.15	0.85	3400	1.35	-48	3800	1.29	+18
	0.20	5.0	9	0.34	0.91	5600	1.88	-22	5000	1.42	+14
	0.29	4.6	28	0.44	0.87	7200	1.75	-19	6700	1.91	+12
	0.40	4.5	24	0.58	0.89	9400	1.96	-2	9200	1.57	+6
	0.49	2.5	19	0.72	0.95	13100	2.05	+20	12300	1.71	+4
	0.61	3.5	20	0.83	0.91	11700	2.29	+31	10100	1.66	+4
	0.67	2.7	16	0.88	0.89	15500	2.37	+41	15100	1.73	+3
	0.81	1.3	8	0.84	0.89	16000	2.46	+56	12200	1.86	+3
	0.90	1.1	9	0.97	0.88	18000	2.47	+67	17900	1.84	+2
1f	0.10	10.2	26	0.23	>0.99	7200	1.18	+341	4100	1.12	+21
	0.50	2.6	21	0.51	>0.99	30600	1.14	+614	10100	2.00	+9

^a Solvent, toluene; $[1 + \text{styrene}] = 0.1 \text{ mol} \cdot \text{L}^{-1}$; $[\text{AIBN}] = 6.0 \text{ mmol} \cdot \text{L}^{-1}$; temp., 60°C . ^b Mole fraction of M_1 in the monomer feed. ^c Mole fraction of M_1 unit in the polymer; determined by ^1H and quantitative ^{13}C NMR spectra. ^d Extent of cyclization determined by ^1H and quantitative ^{13}C NMR spectra. ^e Determined by GPC in THF using polystyrene as a standard. ^f Measured in CHCl_3 at 24°C ($c = 1.0$).

Figure 2. Specific rotation ($[\alpha]_{435}^{24}$, c 1.0 in CHCl_3) versus weight fraction of isolated benzoate diad ($P(1, M_1)$) in copolymers **3a** ($\circ$), **3d** ($\triangle$), **3e** ($\bullet$), and **3h** ($\square$). The $P(1, M_1)$ values were calculated according to eq 1.

isopropylidene-D-glucitol, D-mannitol, and D-iditol corresponding to the 1,2-diol templates, yielded optically active copolymer **3** in the cyclocopolymerization. The templates **g** and **h** having (*R,R*)-configuration form an enantiomeric (*S,S*)-racemo configuration in copolymers **3g** and **3h**. On the other hand, template **i** having (*S,S*)-configuration formed an (*R,R*)-configuration in polymer **3i**. The direction of the ester carbonyl groups in the monomer seriously affected the stereochemistry during the cyclization.¹⁸ When the carbonyl groups are situated each face to face with the *Si* face, the conformer leads to the formation of (*R,R*)-racemo cyclic units and *vice versa*. The suitable conformation of the monomer for cyclization, therefore, is shown in Scheme 2. Monomers **1g** and **1h** give a conformational transformation between **4A** and **4B**, and monomer **1i** involves **5A** $\rightleftharpoons$ **5B** interconversion. The former monomers lead to the formation of (*S,S*)-racemo cyclic units from conformer **4A** and to that of (*R,R*)-racemo units from conformer **4B**. The latter monomer forms (*R,R*)- and (*S,S*)-racemo units from conformers **5A** and **5B**, respectively. The consideration in which **4A** for **1g** and **1h** and **5A** for **1i** are the more suitable conformation for the chirality induction is consistent with the experimental results. Repulsive steric interactions between the 4-vinylbenzoyl group and substituent R_1 or R_2 in the gauche conformation make **4B** and **5B** significantly less stable.

The cyclocopolymerization of monomers **1d**, **1e**, and **1f** with the (*R*)-type templates formed copolymers **3d**, **3e**, and **3f** with the chirality of the (*S,S*)-racemo configuration in the main chain. The occurrence of chirality depended on conformer **5A**. The conformational transformation of **5A** and **5B** was influenced by bulkiness of the substituents in the 1,2-diol templates and the ease of interconversion was concerned to the extent of chirality induction. The extent for the 1,2-diol templates increased with the bulkiness of two substituents R_1 and R_2 in the order of **d** < **a** < **e** = **g** < **f** as shown in Table 1 and Figure 2. Template **f** with two 1-naphtyl groups clearly exceeded template **e**, though the experimental data were insufficient.

The cyclocopolymerization should give four diastereomeric units. Conformers **4A** and **5B** induce the formation of the (*S,R*)-meso units in addition to the (*S,S*)-racemo units, whereas conformers **5A** and **4B** result in the formation of the (*R,S*)-meso units together with the (*R,R*)-racemo units. A desirable design

of the template involves the higher selectivity between two racemo units and the larger depression of meso units. The bulky substituent in the 1,2-diol template was useful for improving the selectivity.

Scheme 2.

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