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Chirality induction in cyclopolymerization: 4. Using three diastereomeric templates, methyl 4,6-*O*-isopropylidene-α-D-gluco-, manno- and altropyranoside in the cyclopolymerization of bis(4-vinylbenzoate) with styrene

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Three distyryl monomers, methyl 4,6-*O*-isopropylidene-2,3-bis-*O*-(4-vinylbenzoyl)-α-D-gluco- (**1a**), altro- (**1b**) and mannopyranoside (**1c**), were prepared. These monomers possess the same configuration except for the torsion angle between the two (4-vinylbenzoyl) groups, which is 60°, −60° and 180° for **1a**, **1b** and **1c** respectively. Their cyclocopolymerizations with styrene (**2**) were carried out using α,α'-azobisisobutyronitrile in toluene at 60°C. The resulting copolymers were hydrolysed using potassium hydroxide in methanol/tetrahydrofuran under reflux and then treated with diazomethane to yield poly(methyl 4-vinylbenzoate-*co*-styrene)s (**4a**, **4b** and **4c**). The copolymer **4a** showed optical activity with a maximum specific rotation ($[\alpha]^{23}_{435}$, $c = 1.0$ in $CHCl_3$) of −6.0°. Copolymers **4b** and **4c** had optical rotations of −1.9° and −2.0° respectively, which were smaller than that of **4a**. The chirality was negative for **1a** and positive for **1b**, and was positive for **4a** and **4b**. On the other hand, **1c** showed a very weak Cotton effect, and the chirality was positive for **4c**. Copyright © 1996 Elsevier Science Ltd.

(Keywords: chirality induction; cyclopolymerization; chiral template; exciton chirality method)

INTRODUCTION

Synthesis of optically active polymers has been interesting in terms of chiral control of the main-chain structure[1,2]. In order to cause asymmetric induction in the main chain, various kinds of chiral elements were used in monomers, catalysts and solvents[3–9]. Using bifunctional monomers with a chiral template in the cyclopolymerization system is one effective method for producing optically active polymers. Wulff realized the synthesis of optically active vinyl polymers with a main-chain chirality through the asymmetric cyclocopolymerization of divinyl monomers possessing a D-mannitol template with achiral monovinyl monomers[10–16]. We also reported the synthesis of optically active poly(methyl methacrylate-*co*-styrene) using 2,3-*O*-isopropylidene-L-threitol as a chiral template[17]. In the previous paper in this series, we obtained optically active poly(methyl 4-vinylbenzoate-*co*-styrene) using a similar procedure and determined the absolute configuration of the main chain using the exciton chirality method[18].

Attention is directed to finding a more effective template for chirality induction in the cyclocopolymerization. The structural characteristics of the chiral template are associated with the distance, the torsion angle, the rotational freedom and the steric crowding between two sites in the two polymerizable groups. In this paper, three kinds of chiral 2,3-diols arising from the pyranosides, D-glucose, D-mannose and D-altrose, which are diastereomers and differ from each other only in the configuration about the C2- and C3-carbon atoms, were selected for stereochemical specificity as templates in the asymmetric cyclocopolymerization. Thus the copolymerization of three divinyl monomers, methyl 2,3-bis-*O*-(4-vinylbenzoyl)-4,6-di-*O*-isopropylidene-α-D-gluco- (**1a**), manno- (**1b**) and altropyranoside (**1c**), with styrene (**2**) was carried out. The resulting copolymers **3a–c** were hydrolysed and methylated with diazomethane to give **4**. *Scheme 1* shows a summary of the reaction paths. The chiral configurations of the monomers and copolymers were analysed by measuring their chiroptical properties, and the asymmetric induction mechanism was examined on the basis of the exciton chirality method.

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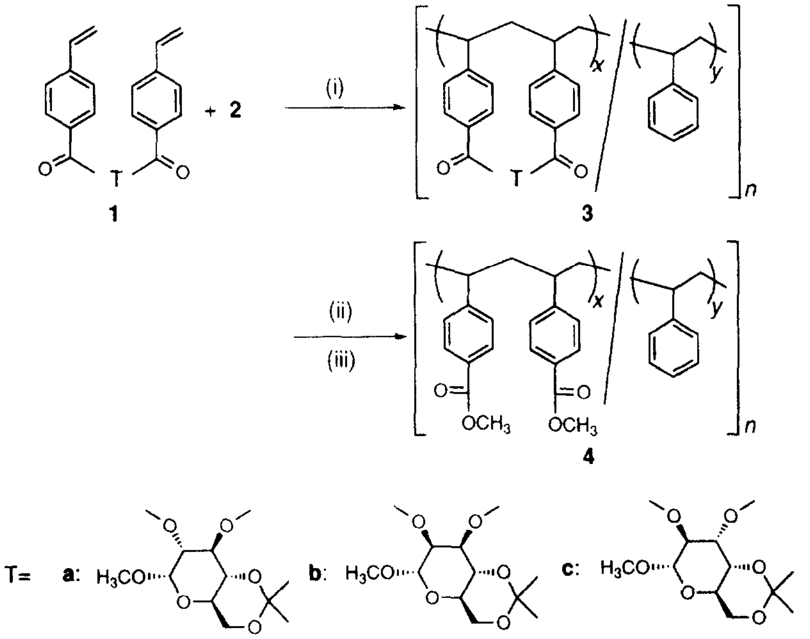


Conditions: (i) AIBN, toluene, 60°C; (ii) KOH, MeOH, reflux; (iii) CH_2N_2, Et_2O

Scheme 1

RESULTS

Cyclocopolymerizations

The radical cyclocopolymerizations of **1a–c** with styrene were carried out using α,α′-azobisisobutyronitrile (AIBN) as an initiator in toluene at 60°C under a nitrogen atmosphere. *Table 1* lists the conditions and experimental results of the copolymerizations of **1a–c** (M_1) and styrene (M_2). The cyclocopolymerization of **1a** proceeded homogeneously, and the resulting copolymers (**3a**) were soluble in common organic solvents such as chloroform and tetrahydrofuran. *Figures 1a* and *1b* show the ^{13}C n.m.r. spectra of the monomer **1a** and the copolymer **3a** respectively. The peaks at 135.9, 116.6 and 116.5 ppm due to the methine and methylene carbons of the vinyl groups in the monomer completely disappeared in the spectrum of the copolymer, and thus any pendant vinyl groups did not remain. This result indicates that the copolymer consists of cyclic repeating units together with those of styrene. The polymer yields were intentionally suppressed so that the composition of the monomer feed reflected the copolymer composition. The mole fractions of M_1 in copolymer (f_1), which were determined from the area ratio of the ^1H n.m.r. peaks between the aromatic and methoxy protons, are plotted vs. the mole fraction of M_1 in the feed (F_1) in *Figure 2a*. The Mayo–Lewis equation was adapted to give the copolymerization parameters of $r_1 = 0.53$ and $r_2 = 0.41$. The number-average molecular weights (M_n) of the copolymers increased with increasing F_1 and ranged from 5300 to 26 100. The specific rotations ($[\alpha]_{435}^{23}$, $c = 1.0$ in $CHCl_3$) increased from +203° to +414° along with an increasing f_1 value from 0.11 to 0.76.

Table 1 Cyclocopolymerization of bis(4-vinylbenzoate) monomers **1a–c** (M_1) with styrene (**2**, M_2) initiated by α,α′-azobisisobutyronitrile (AIBN)[a]

M_1	F_1[b]	Time (h)	Yield (%)	f_1[c]	M_n[d] ($\times 10^{-3}$)	$[\alpha]_{435}^{23}$[e]
1a	0.05	43	15	0.11	5.3	+203
	0.10	14	18	0.18	5.8	+286
	0.20	9	33	0.31	7.0	+343
	0.30	5	32	0.38	9.4	+376
	0.40	4	27	0.46	10.8	+386
	0.50	4	31	0.51	13.7	+402
	0.57	3	26	0.58	14.9	+403
	0.71	2	21	0.67	16.3	+408
	0.79	2	15	0.72	18.6	+414
	0.89	1	15	0.76	26.1	+411
1b	0.10	26	21	0.20	6.3	−171
	0.20	14	33	0.32	8.5	−210
	0.30	7	24	0.42	9.8	−248
	0.40	6	27	0.50	11.3	−263
	0.49	7	38	0.58	15.5	−272
	0.59	4	26	0.63	19.0	−283
	0.69	3	28	0.71	19.9	−293
	0.80	2	18	0.80	24.1	−307
1c	0.19	13	43	–[g]	22.3	−86
	0.39	9	72[f]	–[g]	–[g]	–[g]
	0.59	6	63[f]	–[g]	–[g]	–[g]
	0.78	3	68[f]	–[g]	–[g]	–[g]

[a] All polymerization was carried out at 60°C in toluene under nitrogen atmosphere. Initial total monomer concentration ([**1** + **2**]) was 0.1 mol l^{-1}, and initiator concentration ([AIBN]) was 1.0 g l^{-1}

[b] Mole fraction of **1** in feed

[c] Mole fraction of **1** unit in copolymer **3**, estimated from ^1H n.m.r. spectrum

[d] Determined by g.p.c. in THF using polystyrene as a standard

[e] Measured in $CHCl_3$, $c = 1.0$

[f] Insoluble in $CHCl_3$ and THF

[g] Not determined

The copolymerization of **1b** and styrene also proceeded homogeneously and the resulting copolymers **3b** were soluble in common organic solvents. No residual vinyl groups were observed in the ^{13}C n.m.r. spectrum of copolymer **3b**, and the extent of cyclization was 100% as in the case of **1a**. *Figure 2b* shows the copolymer composition curve fitting the copolymerization parameters of $r_1 = 0.85$ and $r_2 = 0.38$, and the M_n of **3b** were ranged from 6300 to 24 100. The specific rotations ($[\alpha]_{435}^{23}$, $c = 1.0$ in $CHCl_3$) varied from −171° to −307° with the copolymer composition.

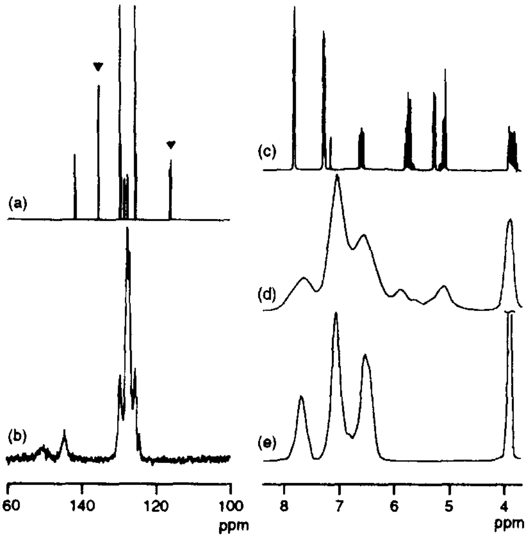


Figure 1 ^{13}C n.m.r. spectra of (a) monomer **1a** and (b) copolymer **3a** ($x/y = 0.18/0.82$), and ^{1}H n.m.r. spectra of (c) monomer **1a**, (d) copolymer **3a** ($x/y = 0.18/0.82$) and (e) hydrolysed copolymer **4a** ($x/y = 0.18/0.82$). All spectra were measured in $CDCl_3$ at 21°C

Table 2 Hydrolysis and methylation of **3** to **4**[a]

	3			**4**		
				M_n		
	f_1[b]	M_n[b] ($\times 10^{-3}$)	$[\alpha]_{435}$[b]	Calc.[c]	Obs.[d]	$[\alpha]_{435}$[e]
3a	0.11	5.3	+203	4.6	4.1	−4.2
	0.18	5.8	+286	4.8	4.1	−6.0
	0.31	7.0	+343	5.4	4.5	−4.7
	0.38	9.4	+376	7.0	6.2	−3.0
	0.46	10.8	+386	7.8	8.1	−1.6
	0.67	16.3	+408	11.2	11.5	−1.1
3b	0.20	6.3	−203	5.1	5.2	−1.1
	0.32	8.5	−286	6.5	5.6	−1.7
	0.42	9.8	−343	7.2	6.2	−1.9
	0.71	19.9	−376	13.6	10.7	−0.1
3c	0.38[f]	22.3	−86	16.5	4.4	+2.1
	0.55[f]	–	–	–	7.1	+1.2
	0.72[f]	–	–	–	8.4	+0.9
	0.81[f]	–	–	–	8.9	+0.6

[a] Reaction conditions are described in the Experimental section (see Appendix)
[b] Data from *Table 1*
[c] Calculated from f_1 and M_n of **3**
[d] Determined by g.p.c. using polystyrene as a standard
[e] Measured in $CHCl_3$, $c = 1.0$
[f] Mole fraction of **1** units in copolymer **4c**

The copolymerization system for **1c** was heterogeneous and the resulting copolymers **3c** were insoluble in common organic solvents. Monomer **1c** tended to form a gel during the copolymerization process, but a soluble polymer was obtained only under the condition of $F_1 = 0.19$. The ^{1}H and ^{13}C n.m.r. of the soluble copolymer showed small peaks due to the vinyl groups. The M_n of the soluble polymers was 22 300 and the specific rotation ($[\alpha]_{435}^{23}$, $c = 1.0$ in $CHCl_3$) was −85.7°. The M_n of **3c** obtained with $F_1 = 0.19$ was remarkably higher than those for **3a** and **3b** with a similar F_1, which suggests that the cross-linking reaction occurred slightly even though a soluble copolymer for **3c** was formed.

Removal of templates

The removal of the templates from **3a–c** was carried out by alkali hydrolysis using KOH and was followed by methylation with diazomethane to give poly(methyl 4-vinylbenzoate-*co*-styrene)s (**4a–c**). *Figures 1c*, *1d* and *1e* show the ^{1}H n.m.r. spectra of **1a**, **3a** and **4a** respectively. Because the absorption at 5.3–5.6 ppm due to the anomeric methyl protons disappeared after hydrolysis, the removal of the template was achieved completely. For the copolymers **4b** and **4c**, the templates were removed as well. *Table 2* shows the results of hydrolysis and methylation. The calculated M_n for **4** were estimated from the values of M_n and f_1 for **3**. Copolymers **4a–c** were white powders and were soluble in chloroform and tetrahydrofuran.

The observed values of M_n for **4a** varied from 4100 to 11 500 along with the copolymer composition, which agreed well with the calculated values for **3a**. This indicates that there are no unexpected reactions, such as degradation of the polymer main chain, through the conversion from **3a** to **4a**. This also suggests the high extent of cyclization of **1a**, because cross-linking should reduce the M_n from the calculated values. For **4b**, the observed M_n also satisfactorily agreed with the calculated values. On the other hand, the M_n of 4400 for **4c** was almost one-fourth of the calculated value of 16 500. This indicates that a cross-linking reaction occurred during the cyclocopolymerization of **1c** and styrene.

Copolymer **4a** exhibited optical activity with specific rotations ($[\alpha]_{435}^{23}$, $c = 1.0$ in $CHCl_3$) from −1.1° to −6.0°,

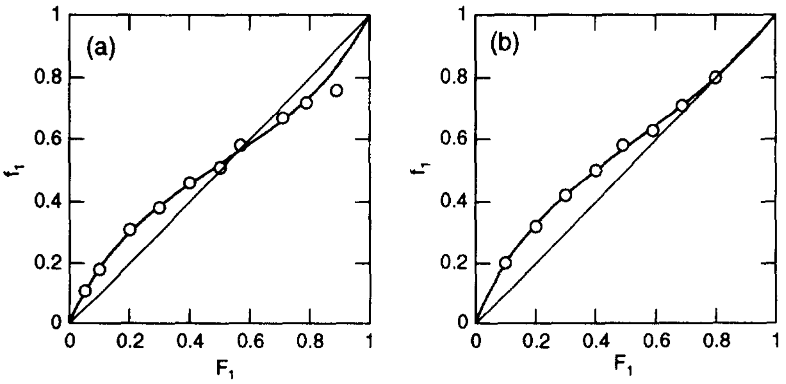


Figure 2 Copolymer composition curves for the radical copolymerization of (a) **1a** and (b) **1b** with styrene, using AIBN as an initiator in toluene at 60°C

the sign of which is opposite that for copolymer **3a**. Copolymers **4b** and **4c** also showed specific rotations from −0.1° to −1.9° and from +0.6° to +2.1°, respectively, which values were smaller than those for **4a**. After **4** was prepared by the hydrolysis of **3**, the sign of the optical rotation was opposite for **3c/4c** but the same for **3b/4b**.

DISCUSSION

The difference in stereochemistry among monomers **1a–c** should affect the cyclopolymerization tendency and the efficiency of asymmetric induction. Therefore the configuration of the two 4-vinylbenzoate groups needs to be clarified, and for this purpose the exciton chirality method based on the c.d. measurement is applicable to the monomer system. Nakanishi *et al.* define that the split Cotton effect with first positive and second negative Cotton effects is a positive chirality and that with first negative and second positive Cotton effects is a negative one[19,20]. According to the exciton chirality method, the maximum wavelength (λ_{max}) of the u.v. spectrum depends on the dihedral angle between two chromophores[21]. In addition, the *A* value, the c.d. amplitude of exciton Cotton effects, is inversely proportional to the square of the distance between two chromophores[22].

For monomers **1a–c**, the isopropylidene group attached at the 4,6-*O*- positions of methyl α-D-gluco-, α-D-manno- and α-D-altropyranosides is in the *trans* configuration. The *trans*-fused isopropylidene group at the 4,6-*O*- positions of the pyranoside ring results in greater conformational stability, and thus the ring structure in solution is the *trans*-decalin type conformation. These templates, therefore, are assigned the C_1^4 conformation as shown in *Scheme 2*. The dihedral angle between the C–O bonds at C2 and C3 is $\phi = 60°$ for the glucopyranoside of **1a**, $\phi = -60°$ for the mannopyranoside of **1b** and $\phi = 180°$ for the altropyranoside of **1c**. The u.v. and c.d. spectra of the monomers are shown in *Figure 3*, and the chiroptical properties are summarized in *Table 3*. Monomers **1a**, **1b** and **1c** have λ_{max} at 273.5, 272.2 and 277.0 nm respectively, and these values reflect the dihedral angle between the two benzoate groups. The benzoate chromophore in **1a** gives a typical split Cotton effect consisting of a positive first Cotton effect and negative second Cotton effect. The twist of the two benzoate groups is thus in a clockwise direction; i.e., the chirality is positive. Because the c.d. spectrum exhibits a split Cotton effect with first negative and second positive Cotton effects, the chirality is positive for **1b**, which is opposite that for **1a**. These chiralities correspond to the direction of the angle between the two 4-vinylbenzoate groups. On the other hand, because **1c** shows a very

Table 3 Summary of c.d. and u.v. spectra of monomers **1a–c**[a]

	U.v.		C.d.		
Monomer	ϵ $(\times 10^{-5})$	λ_{max} (nm)	$\Delta\epsilon$	A	λ (nm)
1a	4.59	274	+41.9 −27.4	69.3	284 261
1b	5.02	272	−43.2 +16.3	59.5	284 260
1c	4.48	277	−7.7		283

[a] All spectra were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 21°C. Sample concentrations were 4.65, 3.96 and 7.67×10^{-5} mol l^{-1} for **1a**, **1b** and **1c** respectively

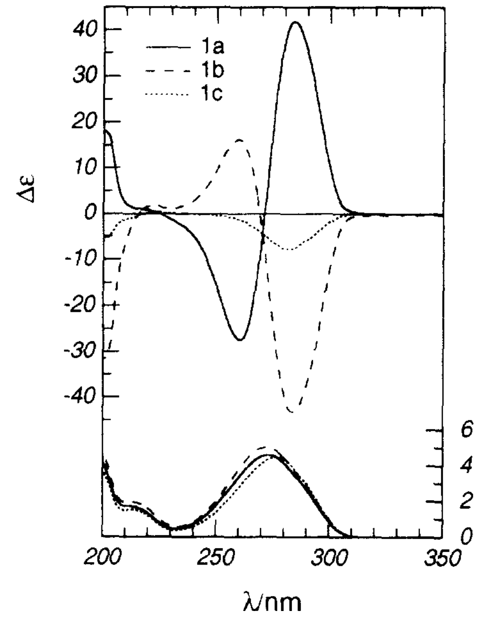
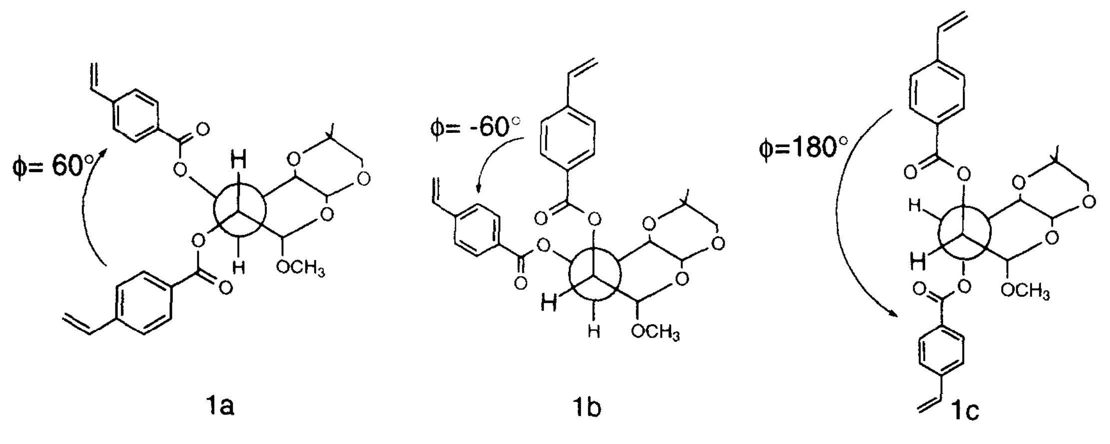


Figure 3 C.d. and u.v. spectra of monomers **1a**, **1b** and **1c**. All spectra were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 21°C



Scheme 2

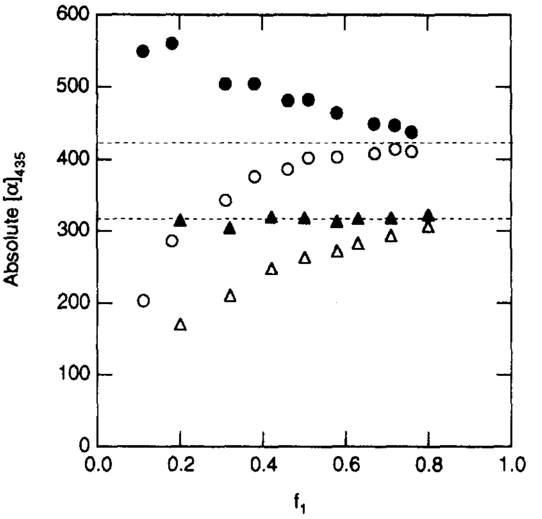


Figure 4 Specific rotations ($[\alpha]^{23}_{435}$) of copolymers **3a** (○) and **3b** (△), and ($[\alpha]^{23}_{435}/w_1$) of **3a** (●) and **3b** (▲)

weak Cotton effect, the conformation between the two 4-vinylbenzoate groups is slightly distorted even though the predicted dihedral angle of $\phi = 180°$.

The extent of cyclization for monomers **1a** and **1b** in the resulting copolymers was 100%, because the characteristic absorption due to the vinyl groups disappeared in the n.m.r. spectra of copolymers **3a** and **3b**. Thus the dihedral angles between the two 4-vinylbenzoate groups of $\phi = 60°$ and $-60°$ are favourable for intramolecular cyclization, which was inhibited little by incorporating the comonomer styrene. On the other hand, monomer **1c** was characterized by a higher gelation tendency in the polymerization process, which is caused by the dihedral angle of $\phi = 180°$ in the pyranoside template.

Figure 4 shows the variations in specific rotation $[\alpha]^{20}_{435}$ with the mole fraction of M_1 units (f_1) in copolymers **3a** and **3b**. The specific rotation noticeably increased with increasing f_1 for both copolymer systems and the curves were asymptotic relative to the values for the homopolymers. The occurrence of induced optical activity in the cyclopolymerization is estimated from the specific rotation per weight fraction of M_1 units ($[\alpha]^{23}_{435}/w_1$) (*Figure 4*). For the copolymer system of **3a**, the values of $[\alpha]^{23}_{435}/w_1$ increased along with decreasing f_1. This result indicates that a new chirality was induced in copolymer **3a**. In contrast, for **3b**, the values of $[\alpha]^{23}_{435}/w_1$ were approximately consistent in the whole range of f_1, and thus the expectation for chirality induction is somewhat obscured.

Copolymer **4a** exhibited optical activity with specific rotation in the range from $-4.2°$ to $-1.1°$. The sign of these values is opposite to those for polymer **3a**, thereby indicating that a new chirality was induced in the main chain due to the **1a** unit. The c.d. spectrum of copolymer **4a** is shown in *Figure 5*. The dibenzoate chromophore in **4a** shows a split Cotton effect consisting of negative first and positive second Cotton effects. Because the chirality is negative for copolymer **4a** and positive for monomer **1a**, the configurational change is obvious in the polymerization process. The α-D-glucopyranoside template, having an *S*,*S*-configuration, induced the new chirality in the intramolecular cyclization of **1a** to form an enantiomeric *R*,*R-racemo* main chain. For the copolymerization of 2,3-bis-*O*-(4-vinylbenzoyl)-1,4-*O*-isopropylidene-L-threitol and styrene, the chiroptical property of c.d. measurement for the monomer and cyclopolymer was opposite that for the template-free polymer with an *S*,*S-racemo* configuration in the main chain. This was opposite to the result using the α-D-glucopyranoside template.

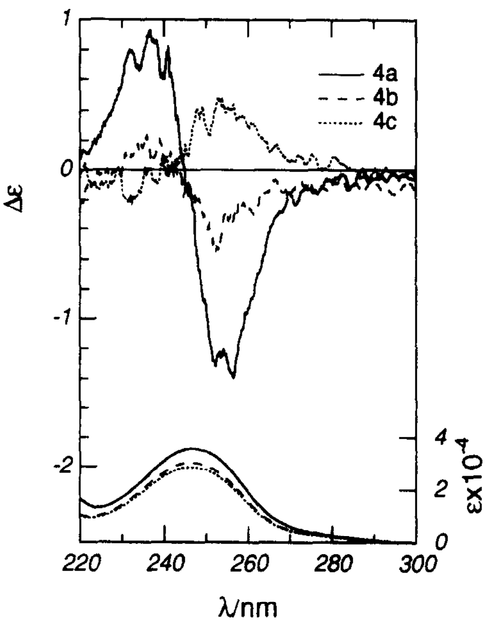


Figure 5 C.d. and u.v. spectra of polymers **4a** ($x/y = 0.18/0.82$), **4b** (0.20/0.80) and **4c**. All spectra were recorded in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) at 21°C. The $\Delta\epsilon$ values were based on the concentration of methyl *p*-vinylbenzoate units, calculated using the copolymer compositions

Copolymer **4b** is optically active, though the absolute values of the specific rotation are small. The c.d. spectrum exhibits a relatively weak split Cotton effect (*Figure 5*), and the chirality is negative for **4b**. Because the same chirality is found for **1b** and **4b**, the manner of asymmetric induction due to the twist in the template for **1b** is different from that for **1a**. For **1a** and **1b**, the dihedral angle of the two 4-vinylbenzoate groups is in the opposite direction but has the same absolute value. The λ_{max} values of the u.v. spectra and the amplitudes of the split c.d. curves, the *A* values (*Table 3*), indicate that the dihedral angle for **1b** is smaller than that for **1a** and the distance between the two 4-vinylbenzoate groups for **1b** is larger than that for **1a**. The chiroptical property for **1a** and **1b** is expected such that each chirality for the monomer changes to the opposite one for the template-free, optically active polymer, although with a different efficiency for asymmetric induction. This assumption was confirmed in previous studies using L-threitol, D-mannitol, D-glucitol, 1,3-(*S*)-butanediol and 2,4-(2*S*,4*S*)-pentanediol templates. The result for **1b** is therefore the first example in which the chirality does not change from the monomer to the polymer; thus further study is needed to clarify the template effect of mannopyranoside.

Copolymer **4c** has a small absolute value of the specific rotation. The relatively weak Cotton effect in **4c** (*Figure 5*) suggests that the dibenzoate groups are distorted to be able to form the cyclized units. Although the second Cotton effect is too weak to be observed, the first Cotton effect is positive. The chirality of polymer **4c** is positive, which reflects the chiral twist of **1c**.

CONCLUDING REMARKS

Methyl 4,6-*O*-isopropylidene-2,3-bis-*O*-(4-vinylbenzoyl)-α-D-gluco- (**1a**), manno- (**1b**) and altropyranoside (**1c**), which possess a torsion angle between the two (4-vinylbenzoyl) groups of 60°, −60° and 180° respectively, were copolymerized with styrene using AIBN. For **1a** and **1b**, the resulting copolymers were soluble in common organic solvents and the extent of cyclization was 100%. On the other hand, **1c** tended to form insoluble gel polymers. The template-free polymer, poly(methyl 4-vinylbenzoate-*co*-styrene) (**4**), exhibited optical activity with specific rotations ($[\alpha]^{23}_{435}$, $c = 1.0$ in $CHCl_3$) from −1.1° to −6.0° for **1a**, from −0.1° to −1.9° for **1b** and from +0.6° to +2.1° for **1c**. The negative chirality for **1a** transmitted its chiral twist to **4a** with a positive chirality. On the other hand, the chirality was the same for **1b** and **4b**, which was the first example in which the chirality does not change from the monomer to the polymer. In addition, **1c** showed a very weak split Cotton effect, indicating that the conformation between the two 4-vinylbenzoate groups was slightly distorted even though the predicted dihedral angle of $\phi = 180°$. This caused a lower optical activity for **4c**.

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APPENDIX: EXPERIMENTAL

Measurements

^1H and ^{13}C n.m.r. spectra were recorded with a JEOL A400II and a JEOL EX270 instrument. U.v. spectra were recorded on a Jasco 660 UV/VIS spectrophotometer. The molecular weight of the resulting polymers was measured by gel permeation chromatography (g.p.c.) in tetrahydrofuran on a Waters M45 high-performance liquid chromatograph equipped with three polystyrene gel columns (Shodex KF-804L). The number-averaged molecular weight (M_n) was calculated on the basis of a polystyrene calibration. Optical rotations were determined with a Jasco DIP-140 digital polarimeter. C.d. spectra were measured at 20°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

Methyl 4,6-*O*-isopropylidene-α-D-gluco-[23], altro-[24] and mannopyranosides[25] were prepared according to the procedure reported. Toluene and benzene were refluxed over sodium-benzophenone ketyl and distilled just before use. Pyridine was distilled from CaH_2. α,α′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Hexafluoroisopropyl alcohol was obtained from Central Glass Co. and used without further purification.

Methyl 4,6-O-isopropylidene-2,3-bis-O-(4-vinylbenzoyl)-α-D-glucopyranoside (1a). A solution of methyl 4,6-*O*-isopropylidene-α-D-glucopyranoside (10 g, 0.043 mol) in pyridine (250 ml) was cooled to 5°C in an ice bath. To this solution, 4-vinyl benzoyl chloride[26] (16 g, 0.096 mol) was added gradually so that the temperature of solution did not rise over 10°C. The reaction mixture was stirred at 80°C for 4 h in an oil bath. After the mixture had cooled to room temperature, 200 ml of water was added. The resulting brown solution was stirred for 1 h and extracted with three portions of 150 ml of diethyl ether. The extract was successively washed with 0.5 M aqueous HCl, 5% aqueous NaOH, and water, and dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, chromatography on silica gel (Kiesel Gel 60, 200-470 mesh, Merck) with benzene/ethyl acetate (95/5, v/v) gave **1a** as a white solid. Yield 8.6 g (0.017 mol, 40%), $[\alpha]_{577} = +241°$ (c 1.0, $CHCl_3$). ^1H n.m.r. (400 MHz, $CDCl_3$): $\delta = 7.93$ (d, $^3J = 8.3$ Hz, 2H, Ar), 7.92 (d, $^3J = 8.3$ Hz, 2H, Ar), 7.38 (d, $^3J = 8.5$ Hz, 2H, Ar), 7.37 (d, $^3J = 8.8$ Hz, 2H, Ar), 6.69 (dd, $^3J_{trans} = 17.7$ Hz, $^3J_{cis} = 11.0$ Hz, 1H, =CH−), 6.68

(dd, $^{3}J_{trans} = 17.6$ Hz, $^{3}J_{cis} = 11.0$ Hz, 1H, =CH−), 5.86 (m, 1H, H(3)), 5.81 (d, $^{3}J_{trans} = 17.7$ Hz, 1H, $=CH_2$), 5.80 (d, $^{3}J_{trans} = 17.7$ Hz, 1H, $=CH_2$), 5.34 (d, $^{3}J_{cis} = 11.0$ Hz, 1H, $=CH_2$), 5.33 (d, $^{3}J_{cis} = 11.0$ Hz, 1H, $=CH_2$), 5.17 (dd, $^{3}J_{2,3} = 9.8$ Hz, $^{3}J_{1,2} = 3.9$ Hz, 1H, H(2)), 5.13 (d, $^{3}J_{1,2} = 3.7$ Hz, 1H, H(1)), 3.98–3.78 (m, 4H, H(4), H(5), and H(6)), 3.40 (s, 3H, OCH_3), 1.49 (s, 3H, CH_3), 1.38 (s, 3H, CH_3). ^{13}C n.m.r. (125 MHz, $CDCl_3$): $\delta = 165.7$, 165.4 (C=O), 142.3, 130.2, 130.0, 129.0, 128.1, 126.1, 126.0 (arom), 135.9 (=CH−), 116.6, 116.5 (CH_2=), 99.8 (C(7)), 97.8 (C(1)), 72.6 (C(2)), 72.2 (C(4)), 69.9 (C(3)), 63.4 (C(5)), 62.4 (C(6)), 55.4 (OCH_3), 29.0, 19.0 (CH_3). Anal. calcd for $C_{28}H_{30}O_8$ (494.5): C 67.99; H 6.12. Found: C 68.13; H 6.14.

*Methyl 4,6-*O*-isopropylidene-2,3-bis-*O*-(4-vinylbenzoyl)-α-D-mannopyranoside (**1b**).* The same procedure as for **1a** was applied to methyl 4,6-*O*-isopropylidene-α-D-mannopyranoside (4.7 g, 0.020 mol), 4-vinyl benzoyl chloride (7 g, 0.042 mol) and 150 ml of pyridine. The crude product was purified by column chromatography on silica gel (Kiesel Gel 60, 200–470 mesh, Merck) with benzene/ethyl acetate (95/5, v/v) to give **1b** as a white solid. Yield 5.4 g (0.011 mol, 55%), $[\alpha]_{577} = -197°$ (*c* 1.0, $CHCl_3$). ^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 8.00$ (d, $^{3}J = 8.5$ Hz, 2H, Ar), 7.85 (d, $^{3}J = 8.3$ Hz, 2H, Ar), 7.51 (d, $^{3}J = 8.3$ Hz, 2H, Ar), 7.35 (d, $^{3}J = 8.0$ Hz, 2H, Ar), 6.78 (dd, $^{3}J_{trans} = 17.6$ Hz, $^{3}J_{cis} = 11.0$, 1H, =CH−), 6.70 (dd, $^{3}J_{trans} = 17.7$ Hz, $^{3}J_{cis} = 11.0$ Hz, 1H, =CH−), 5.90 (d, $^{3}J_{trans} = 17.6$ Hz, 1H, $=CH_2$), 5.80 (d, $^{3}J_{trans} = 17.6$ Hz, 1H, $=CH_2$), 5.63 (dd, $^{3}J_{2,3} = 3.6$ Hz, $^{3}J_{1,2} = 1.7$ Hz, 1H, H(2)), 5.59 (dd, $^{3}J_{3,4} = 9.9$ Hz, $^{3}J_{2,3} = 3.6$ Hz, 1H, H(3)), 5.43 (d, $^{3}J_{cis} = 11.0$, 1H, $=CH_2$), 5.34 (d, $^{3}J_{cis} = 11.0$ Hz, 1H, $=CH_2$), 4.84 (d, $^{3}J_{1,2} = 1.5$ Hz, 1H, H(1)), 4.34–4.30 (m, 1H, H(4)), 3.97–3.88 (m, 3H, H(5) and H(6)). 3.45 (s, 3H, OCH_3), 1.56 (s, 3H, CH_3), 1.39 (s, 3H, CH_3). ^{13}C n.m.r. (125 MHz, $CDCl_3$): $\delta = 165.1$ (C=O), 142.4, 142.0, 130.1, 130.0, 129.0, 128.6, 126.3, 126.0 (arom), 136.0, 135.9 (=CH−), 116.9, 116.5 ($=CH_2$), 100.0 (C(7)), 99.7 (C(1)), 70.8 (C(2)), 69.4 (C(4)), 69.3 (C(3)), 64.7 (C(5)), 62.4 (C(6)), 55.2 (OCH_3), 29.1, 19.2 (CH_3). Anal. calcd for $C_{28}H_{30}O_8$ (494.5): C 67.99; H 6.12. Found: C 68.29; H 6.21.

*Methyl 4,6-*O*-isopropylidene-2,3-bis-*O*-(4-vinylbenzoyl)-α-D-altropyranoside (**1c**).* The same procedure as for **1a** was applied to methyl 4,6-*O*-isopropylidene-α-D-altropyranoside (3.1 g, 0.013 mol), 4-vinyl benzoyl chloride (4.5 g, 0.027 mol) and 100 ml of pyridine. The crude product was purified by column chromatography on silica gel (Kiesel Gel 60, 200–470 mesh, Merck) with benzene/ethyl acetate (97/3, v/v) to give **1c** as a white solid. Yield 3.3 g (0.007 mol, 51%), $[\alpha]_{577} = -40°$ (*c* 1.0, $CHCl_3$). ^{1}H n.m.r. (400 MHz, $CDCl_3$): $\delta = 8.08$ (d, $^{3}J = 8.5$ Hz, 2H, Ar), 8.02 (d, $^{3}J = 8.3$ Hz, 2H, Ar), 7.50 (d, $^{3}J = 8.3$ Hz, 2H, Ar), 7.49 (d, $^{3}J = 8.3$ Hz, 2H, Ar), 6.77 (dd, $^{3}J_{trans} = 17.6$ Hz, $^{3}J_{cis} = 11.0$ Hz, 2H, =CH−), 5.89, 5.88 (dd, $^{3}J_{trans} = 17.7$ Hz, $^{3}J = 0.73$ Hz, 2H, $=CH_2$), 5.49 (m, 1H, H(3)), 5.41 (m, 2H, $=CH_2$), 5.31 (dd, $^{3}J_{1,2} = 3.1$ Hz, $^{3}J_{2,3} = 0.73$ Hz, 1H, H(2)), 4.77 (d, $^{3}J_{1,2} = 0.49$ Hz, 1H, H(1)), 4.39–4.32 (m, 1H, H(5)), 4.22 (dd, $^{3}J_{4,5} = 10.0$ Hz, $^{3}J_{3,4} = 3.2$ Hz, 1H, H(4)), 3.99 (m, 1H, H(6)), 3.89 (m, 1H, H(6)), 3.45 (s, 3H, OCH_3), 1.58 (s, 3H, CH_3), 1.35 (s, 3H, CH_3). ^{13}C n.m.r. (125 MHz, $CDCl_3$): $\delta = 165.2$, 164.6 (C=O), 142.6, 142.1, 130.3, 130.2, 129.2, 128.3, 126.3, 126.1 (arom), 136.1, 135.9 (=CH−), 117.0, 116.5 (CH_2=), 99.9 (C(7)), 98.9 (C(1)), 70.3 (C(2)), 68.0 (C(4)), 67.6 (C(3)), 62.5 (C(6)), 59.7 (C(5)), 55.6 (OCH_3), 29.0, 19.0 (CH_3). Anal. calcd for $C_{28}H_{30}O_8$ (494.5): C 67.99; H 6.12. Found: C 68.00; H 6.13.

Copolymerization

Copolymerizations were performed in a dried glass ampoule under N_2 atmosphere. A typical procedure is as follows. **1a** (0.831 g, 1.68 mmol), styrene (0.175 g, 1.68 mmol), AIBN (34 mg) and dry toluene (33.6 ml) were placed in the glass ampoule. 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 4 h, the polymerization mixture was poured into methanol (340 ml) and the precipitate was filtered. The white powder obtained was reprecipitated with chloroform–methanol and dried *in vacuo*. Yield: 0.31 g (31%). The comonomer composition was 0.51/0.49 (**1a**/styrene), which was estimated from the area ratio of the aromatic and aliphatic regions in the ^{1}H n.m.r. spectrum.

Alkali hydrolysis of copolymers 3

A typical procedure is as follows. The solution **3a** (0.10 g, **1a**/styrene = 0.51/0.49) in THF (4 ml) was placed in a Teflon bottle equipped with a reflux condenser. To this, 25% methanolic KOH (50 eq. to C=O group in copolymer) was added. The reaction mixture was refluxed for 50 h with the addition of a small portion of water several times. After neutralization with diluted hydrochloric acid while cooling in an ice bath, the mixture was transferred to a cellulose tube and dialysed 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 the hydrolysed copolymers to 4

A typical procedure is as follows. To a mixture of the 0.5 M diazomethane ethereal solution[27] (60 ml, 30 mmol) and benzene (60 ml), a finely divided copolymer **4a** (**1a**/styrene = 0.51/0.49) (62 mg, 0.88 mmol of C=O group) was added. The polymer was dissolved, with evolution of N_2 gas. The mixture was allowed to stand for 14 h at room temperature, and the solvents were removed under reduced pressure. The residue was dissolved in 0.5 ml of $CHCl_3$, and the solution was poured into 50 ml of methanol. The white precipitate was filtered and dried *in vacuo*. Yield: 61 mg (97%).