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Chirality Induction in Cyclopolymerization. 8. Cyclocopolymerization of 1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol with Styrene

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ABSTRACT: Radical cyclocopolymerization of the dimethacrylate **1** (M_1), which was derived from 1,2:5,6-di-*O*-isopropylidene-D-mannitol, with styrene (M_2) induced new chirality in the polymer chain. The removal of the chiral template in the copolymer **2** followed by treatment with diazomethane gave optically active poly(methyl methacrylate-*co*-styrene) (**4**). Polymer **4** had more active chirality upon increasing the M_1 unit, thus indicating that the new chirality should be induced by the M_1 diad unit rather than the isolated M_1 unit. Characteristics of monomer **1** include the considerably higher fraction of tactic triad *rr* in poly(methyl methacrylate) (PMMA) derived from the homopolymerization and the larger probability of forming the racemo diad of the M_1 unit during the intermolecular reaction of the copolymerization. In polymer **4**, the origin of chirality was assigned to the chiral tetrad sequences of the MMA unit which were induced by participation of the racemo configuration.

Introduction

A new aspect of polymer synthesis is the fine construction of the main chain. One of the problems is chirality induction into the main chain, that is, asymmetric polymerization. The cyclocopolymerization capable of forming the chiral diad without mirror planes affords a useful method for the asymmetric polymerization.[1] Wulff et al. synthetically realized the chirality induction during the cyclocopolymerization of the chiral bifunctional monomers, bis(4-vinylphenyl)boronate[2−6] and bis[4-[(methacryloyl)oxy]phenyl]boronate[7] carrying a 3,4-*O*-cyclohexylidene-D-mannitol template, with achiral monomers. We have also reported the cyclocopolymerization of dimethacrylate[8] and bis(4-vinylbenzoate)[9−14] having saccharide moieties with styrene to yield optically active poly(methyl methacrylate-*co*-styrene) and poly(methyl 4-vinylbenzoate-*co*-styrene).

The cyclocopolymerization of 2,3-*O*-isopropylidene-1,4-di-*O*-methacryloyl-L-threitol with styrene yielded poly(methacrylic acid-*co*-styrene) which became optically active with an increasing fraction of comonomer units.[8] The bis(4-vinylbenzoate) monomers were useful for determining the absolute configuration of the cyclic units using the exciton chirality method.[9] The chirality of dibenzoate showed the configurational change in the polymerization process, and thus the template transmitted its chirality to the main chain during the intramolecular cyclization to form an enantiomeric cyclic unit.

In this paper, the characteristics of the dimethacrylate monomer (M_1) having D-mannitol as the chiral template during the cyclocopolymerization with styrene (M_2) are presented. As is distinct from the known cases[4,7,8,14] in which the isolated M_1 unit participates in the occurrence of chirality, the copolymer after cleaving the template became more active in chirality with increasing M_1 unit in the copolymer before hydrolysis. The origin of chirality is interpreted as being assigned to the chiral tetrad sequences.

Experimental Section

1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol (1). 1,2:5,6-Di-*O*-isopropylidene-D-mannitol[15] (13.1 g, 50 mmol) was dissolved in anhydrous pyridine (130 mL) and then methacryloyl chloride (12.5 g, 120 mmol) was added with ice-cooling. The mixture was heated at 70 °C for 7 h and then allowed to stand overnight at room temperature. The entire mixture was poured into water and then extracted with ether. After removal of the solvent, the resulting oil was purified by column chromatography on silica gel with hexane/ether (vol ratio 7:3) to yield a colorless crystal. The product had mp 53 °C after recrystallization with hexane (5.1 g, 26%): $[\alpha]_{435}$ $+79.7°$ and $[\alpha]_D$ $+38.8°$ (c 1.0 in $CHCl_3$ at 24 °C); ^1H NMR (270 MHz, $CDCl_3$) δ 6.15 (s, 2H), 5.64 (s, 2H), 5.43 (dd, $^3J = 2.5$ Hz, $^3J = 7.8$ Hz, 2H), 4.27−4.21 (m, 2H), 3.97−3.86 (m, 4H), 1.96 (s, 6H), 1.35 (s, 6H), and 1.31 ppm (s, 6H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 166.0 (C=O), 135.6 (C=), 126.6 (=CH_2), 109.3 (C), 74.7 (CH), 71.6 (CH), 65.5 (CH_2), 26.3 (CH_3), 25.1 (CH_3), and 18.2 ppm (α-CH_3); IR (KBr) ν(cm^{-1}) 1760 (C=O st) and 1636 (C=C st). Anal. Calcd for $C_{20}H_{30}O_8$ (398.45): C, 60.29; H, 7.59. Found: C, 59.99; H, 7.56.

Polymerization. The polymerization was conducted at 60 °C using toluene (45 mL) and azobisisobutyronitrile (AIBN) (46 mg). The total concentration of both monomers was 0.2 $mol \cdot L^{-1}$ in each of the copolymerizations. After an appropriate time for the polymerization, the mixture was poured into a large amount of methanol and a white solid polymer was separated. The obtained polymer was purified from reprecipitation from chloroform−methanol. Conditions, conversions, compositions, and $[\alpha]_{435}$ values are summarized in Table 1.

Cleavage of the Mannitol Template from Polymer 2. To polymer **2** (300 mg) in THF (3 mL) was added 25% methanolic KOH solution (15 mL). The mixture was heated under reflux for 5 h and then converted to be homogeneous by gradually adding water and boiling for ca. 100 h. After neutralization with hydrochloric acid, the solution was dialyzed using a cellophane tube, and later concentrated by freeze-drying, whereupon polymer **3** was obtained.

Poly(methyl methacrylate-*co*-styrene) (4). To a mixture of an ether solution (60 mL) containing diazomethane (ca. 30 mmol) and benzene (60 mL) was added the finely divided polymer **3** (ca. 100 mg; the amount of specimen used corresponded to 1.0 mmol of the C=O group). The polymer was dissolved with evolution of nitrogen gas. The entire mixture was set aside for 14 h and then all the solvent was removed. The residue was purified by reprecipitation (chloroform/methanol).

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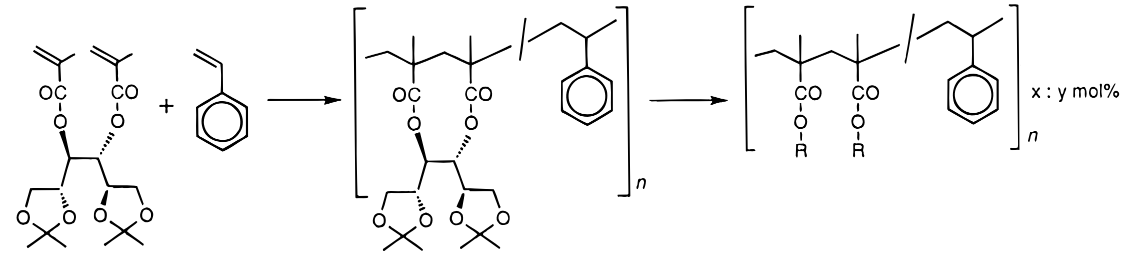
Table 1. Cyclocopolymerization of 1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol (1) (M_1) with Styrene (M_2)[a]

mole fraction of M_1 in feed	time, h	conv %	M_n[b] × 10^{-3}	M_w/M_n[b]	mole fraction of M_1 in copolymer[c]	f_c[d]	$[\alpha]_{435}$[e]
0.05	27	19	4.3	1.64	0.13	1.00	+12.6
0.10	14	14	6.1	1.39	0.21	1.00	+16.9
0.20	10	14	8.5	1.35	0.31	0.96	+19.3
0.30	12	19	8.6	1.45	0.37	0.96	+20.9
0.39	12	19	8.4	1.46	0.43	0.95	+22.8
0.48	9	20	15.7	1.16	0.48	0.94	+23.9
0.60	7	18	14.8	1.41	0.56	0.92	+26.4
0.70	5	18	17.6	1.52	0.62	0.91	+32.0
0.80	6	27	26.6	1.86	0.74	0.89	+39.5
0.90	4	27	41.2	2.66	0.85	0.86	+52.5
1.00[f]	5	53	34.9	20.7	1.00	0.95	+77.9

[a] Conditions: solvent, toluene; $[M_1] + [M_2] = 0.2$ mol·L^{-1}; [AIBN] = 1 g·L^{-1}; temp, 60 °C. [b] Determined by GPC using polystyrene as standard. [c] Determined by ^{1}H NMR spectra. [d] Extent of cyclization. [e] *c* 1.0 in $CHCl_3$ at 24 °C. [f] $[M_1] = 0.1$ mol·L^{-1}.

Scheme 1



1

2

3 : R = H
4 : R = CH_3

Table 2. Effect of Comonomer (M_2) on the Cyclopolymerization Tendency of Monomer 1 (M_1)

$[M_1]$, mol·L^{-1}	$[M_2]$, mol·L^{-1}	f_c[a]
0.10	0.10	0.94
0.10	0	0.95

[a] Extent of cyclization.

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-EX 270 and A 400 II spectrometers in deuterochloroform at 25 °C. The optical rotatory measurements were performed in chloroform at 24 °C using a JASCO DIP 140 digital polarimeter. Molecular weights were determined by gel permeation chromatography (GPC) with a JASCO HPLC system equipped with three polystyrene gel columns (Shodex KF-804L).

Results and Discussion

Copolymerizations of Monomer 1 with Styrene. Radical copolymerizations of monomer **1** (M_1) with styrene (M_2) were performed at 60 °C in toluene using AIBN as the initiator (Scheme 1 and Table 1). The copolymers obtained were colorless powders and soluble in chloroform. The ^{1}H NMR spectral analysis showed that polymer **2** contained a small amount of residual double bonds, which was estimated by the absorptions at δ 5.64 and 6.15 ppm due to the methacrylic groups. The diminution of the absorptions and the formation of the soluble copolymers suggested that the copolymerization proceeded accompanying with the cyclization of monomer **1** to form the 9-membered cyclic units.

During cyclocopolymerization, the intramolecular cyclization of the divinyl monomer is generally inhibited by incorporation of the comonomer. Table 2 shows the effect of the comonomer on the cyclization in the copolymerization of monomer **1** with styrene. The extent of cyclization (f_c) was only slightly influenced by incorporation of the comonomer.

In order to further clarify the effect of the comonomer, the kinetics of the cyclocopolymerization are discussed. The reaction scheme of cyclocopolymerization is given as follows:[16]

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot \quad (1)$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot \quad (2)$$

$$M_1\cdot \xrightarrow{k_C} M_C\cdot \quad (3)$$

$$M_C\cdot + M_1 \xrightarrow{k_{C1}} M_1\cdot \quad (4)$$

$$M_C\cdot + M_2 \xrightarrow{k_{C2}} M_2\cdot \quad (5)$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot \quad (6)$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot \quad (7)$$

Since the intramolecular cyclization of monomer **1** was unaffected by the presence of the comonomer ($k_{12} \rightarrow 0$), the expression of Roovers and Smets[17] can be applied to the copolymer composition relationship.

$$\frac{d[m_1]}{d[m_2]} = \frac{2[M_1]}{[M_2]}\frac{2r_c[M_1] + [M_2]}{2[M_1] + r_2[M_2]}\left(1 + \frac{2[M_1]}{K_c}\right) \quad (8)$$

$$\frac{1}{f_c} = \frac{d[m_1]}{d[m_2]} = 1 + \frac{2[M_1]}{K_c} \quad (9)$$

$$\frac{d[m_c]}{d[m_2]} = \frac{[M_1]}{[M_2]}\frac{r'_1[M_1] + [M_2]}{[M_1] + r'_2[M_2]} \quad (10)$$

where $r_C = k_{C1}/k_{C2}$, $r_2 = k_{21}/k_{22}$, $r'_1 = 2r_C$, $r'_2 = r_2/2$, and $K_C = k_C/k_{11}$.

In Figure 1 the experimental data are plotted according to eq 9. A good straight line was found; the slope gave $K_C = 2.3$ mol·dm^{-3} and a intercept of 1.0, thereby indicating that the comonomer simply acts as a diluent for the intramolecular cyclization of monomer **1**. The K_C value of monomer **1** is comparable to 4.0 mol·dm^{-3} for ethylene glycol dimethacrylate[18] and 3.4 mol·dm^{-3}

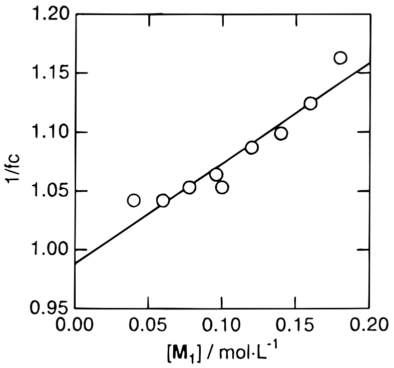


Figure 1. Representation of the experimental data according to eq 9 in the system monomer **1** (M_1)/styrene (M_2).

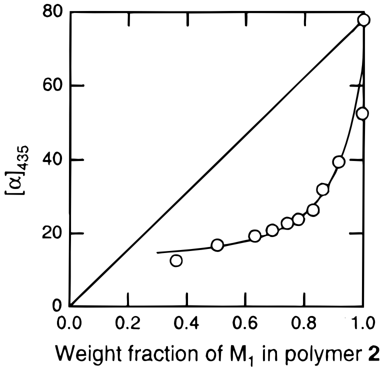


Figure 2. Specific optical rotation ($[\alpha]^{24}_{435}$, *c* 1.0 in $CHCl_3$) versus weight fraction of M_1 in polymer **2**.

for diethylene glycol dimethacrylate[19] during the homopolymerization, thus indicating that monomer **1** has a high tendency for cyclopolymerization. The Kelen–Tüdös plots for the data in Table 1 according to eq 10 gave $r'_1 = 0.35$ and $r'_2 = 0.36$. The parameters r'_1 and r'_2 are the monomer reactivity ratios without consideration of the bifunctionality of monomer **1**.

Chiroptical Properties of Polymers 2 and 4. In Figure 2 the specific rotation ($[\alpha]_{435}$) of polymer **2** showed a deviation from a linear dependence on the weight fraction of M_1 units, resulting from the appearance of new chirality in the polymer.

Polymer **2** was hydrolyzed and the resulting polymer **3** was treated with diazomethane to convert it into the methylated polymer **4**. The removal of the D-mannitol template from polymer **2** was not perfectly performed by treatment with methanolic KOH, because weak resonance signals characteristic of the template spectra were found after hydrolysis.

In spite of the slight residue of the template, the polymers before and after hydrolysis changed the specific rotation from a positive to negative sign, and virtually all of polymer **4** was optically active (Table 3). Figure 3 shows the variation in optical activity of polymer **4** as a function of composition. The absolute value of specific rotation increased with increasing mole fraction of M_1 units in the copolymer. This result indicates that the new chirality should be induced by the M_1 diad and/or triad units rather than the isolated M_1 unit. The chirality induction in the cyclocopolymerizations so far reported was interpreted as being caused by participation of the isolated M_1 unit. The origin of chirality under consideration must be in a different state.

Sequential Analysis of Polymer 4. Polymer **4** is poly(methyl methacrylate-*co*-styrene) [poly(MMA-*co*-St)] of which the structural analysis has already been established by ^1H and ^{13}C NMR spectral methods.[20–22] Figure 4 shows the ^{13}C NMR spectra of the aromatic ipso-carbon and the α-methyl carbon in copolymer **4**. The ipso-carbon resonance was divided into three peaks, X, Y, and Z, and the α-methyl carbon resonance into four peaks, A, B, C, and D. Since the assignments against these peaks are slightly different in the three articles, German's more recent assignment[22] is adopted for the structural analysis of copolymer **4**. The peak areas in the two carbons are as follows:

$$S_A = (\sigma_{MM})^2 F_{MMM} + \sigma_{MM}\sigma_{SM}F_{MMS} \tag{11}$$

$$S_B = \sigma_{MM}(1 - \sigma_{SM})F_{MMS} \tag{12}$$

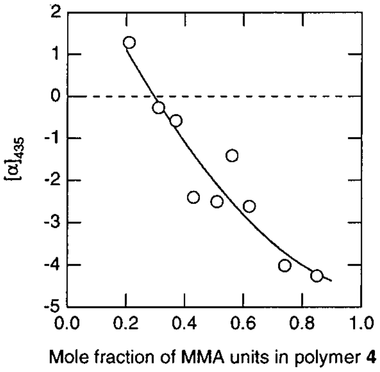


Figure 3. Specific optical rotation ($[\alpha]^{24}_{435}$, *c* 1.0 in $CHCl_3$) versus mole fraction of MMA units in polymer **4**.

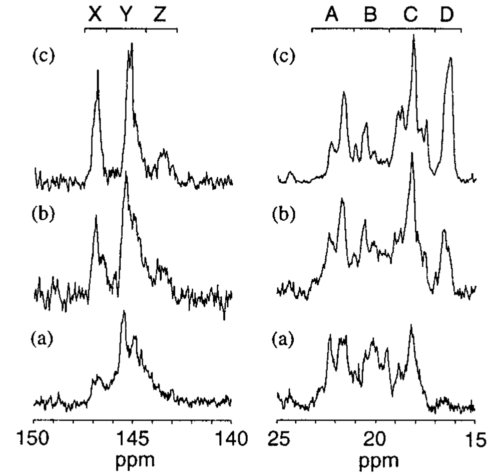


Figure 4. ^{13}C NMR spectra of the α-methyl carbon region (15–25 ppm) and the aromatic ipso-carbon region (140–150 ppm) in polymer **4** with a mole fraction of (a) 0.21, (b) 0.51, and (c) 0.62. The symbols A, B, C, and D and X, Y, and Z denote the divisions of both regions.

Table 3. Chiroptical Property of Polymer 4

mole fraction of M_1 in copolymer	yield[a] %	$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	$[\alpha]_{435}$ [c]
0.21	56	4.2	1.56	+1.29
0.31	41	7.5	1.27	−0.27
0.37		7.3	2.06	−0.58
0.43	46	9.5	1.39	−2.40
0.48	14	6.4	1.87	−2.50
0.56	48	11.8	1.32	−1.41
0.62	72	17.6	1.52	−2.61
0.74	52	18.1	1.69	−4.01
0.85	57	23.2	2.15	−4.25
1.00	21	25.4	2.56	

[a] Based on polymer **2**. [b] Determined by GPC using polystyrene as standard. [c] *c* 1.0 in $CHCl_3$ at 24 °C.

$$S_C = 2\sigma_{MM}(1 - \sigma_{MM})F_{MMM} + (1 - \sigma_{MM})F_{MMS} \quad (13)$$

$$S_D = (1 - \sigma_{MM})^2 F_{MMM} \quad (14)$$

$$S_X = (1 - \sigma_{SM})^2 F_{MSM} \quad (15)$$

$$S_Y = F_{SSS} + (1 - \sigma_{SM})F_{SSM} + 2\sigma_{SM}(1 - \sigma_{SM})F_{MSM} \quad (16)$$

$$S_Z = \sigma_{SM}F_{SSM} + (\sigma_{SM})^2 F_{MSM} \quad (17)$$

where the symbols M and S denote the MMA and the St units, respectively, S_A, S_B, S_C, S_D, S_X, S_Y, and S_Z are the peak areas, σ_{MM} and σ_{SM} are the probability that two adjacent monomer units have a meso configuration, and F_{MMM}, F_{MMS}, F_{MSM}, and F_{SSM} are the population of the monomer sequence triads. Since the perfect cyclization of monomer **1** is reasonably presumed, the population F_{SMS} drops to zero. The equations based on German's assignment, therefore, are simplified as eqs 11−17. The fraction of each peak area in Figure 4 is summarized in Table 4. Although the separation of peaks is unsatisfactory, peaks D and X are preferably used for the analysis. By using eqs 14 and 15, the probabilities σ_{MM} and σ_{SM} may be estimated.

The populations F_{MMM} and F_{MSM} are calculated from the reactivity ratios $r'_1 = 0.35$ and $r'_2 = 0.36$, in the terminal model. The number-average chain length (N) of copolymer **4** is derived from the mole fraction (f_1) of the M_1 units and the chain length (N') in copolymer **2**:

$$N = 2N'f_1 + N'(1 - f_1) = N'(1 + f_1) \quad (18)$$

As the M_1 units in copolymer **2** are converted to the MM diad unit in copolymer **4**, the diad units M_1M_1, M_1M_2, and M_2M_2 produce the sequences MMMM, MMS, and SS, respectively. There is an exact correspondence between the numbers n'_{12} and n_{MMS} of the sequences M_1M_2 and MMS:

$$n_{MMS} = (N - 2)F_{MMS} = (N' - 1)F'_{12} = n'_{12} \quad (19)$$

For a process producing a high polymer, the population F_{MMS} is then

$$F_{MMS} = \frac{N'}{N}F'_{12} = \frac{F'_{12}}{1 + f_1} \quad (20)$$

The sequence $M_1M_2M_1$ quantitatively corresponds to the sequence MSM. Thus,

$$n_{MSM} = (N - 2)F_{MSM} = (N' - 2)F'_{121} = n'_{121} \quad (21)$$

For the larger values of N and N', the population F_{MSM} is given as

$$F_{MSM} = \frac{F'_{121}}{1 + f_1} \quad (22)$$

In a similar manner one obtains

$$F_{SSM} = \frac{F'_{221}}{1 + f_1}$$

$$F_{SSS} = \frac{F'_{222}}{1 + f_1} \quad (23)$$

Table 4. Summary of the Fractions of Peak Areas in ^{13}C NMR Spectra of Polymer 4 [poly(MMA-*co*-St)]

mole fraction of M_1 in copolymer	α-methyl				ipso-C		
	S_A	S_B	S_C	S_D	S_X	S_Y	S_Z
0.21	0.407	0.346	0.243	0.005	0.094	0.856	0.050
0.31	0.375	0.310	0.295	0.020	0.114	0.638	0.248
0.37	0.317	0.334	0.294	0.056	0.208	0.623	0.170
0.43	0.335	0.243	0.354	0.069	0.204	0.667	0.130
0.48	0.315	0.282	0.336	0.066	0.198	0.683	0.119
0.56	0.242	0.186	0.434	0.139	0.258	0.629	0.114
0.62	0.197	0.169	0.419	0.216	0.278	0.562	0.160
0.74	0.157	0.104	0.425	0.314	0.359	0.541	0.100
0.85	0.155	0.109	0.416	0.320	0.391	0.490	0.118

The population F'_{12} of the diad M_1M_2 and populations F'_{121}, F'_{221}, and F'_{222} of the triads $M_1M_2M_1$, $M_2M_2M_1$, and $M_2M_2M_2$ are given by the probabilities P_{11}, P_{12}, P_{21}, and P_{22} forming the diads M_1M_1, M_1M_2, M_2M_1, and M_2M_2, that is,

$$F'_{12} = \frac{2P'_{21}P'_{12}}{P'_{12} + P'_{21}} \qquad F'_{121} = \frac{P'_{21}P'_{12}P'_{21}}{P'_{12} + P'_{21}}$$

$$F'_{221} = \frac{2P'_{12}P'_{22}P'_{21}}{P'_{12} + P'_{21}} \qquad F'_{222} = \frac{P'_{12}P'_{22}P'_{22}}{P'_{12} + P'_{21}} \quad (24)$$

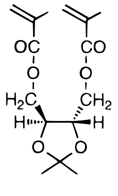
The probabilities are given by

$$P'_{12} = \frac{[M_2]}{r'_1[M_1] + [M_2]} = 1 - P'_{11},$$

$$P'_{21} = \frac{[M_1]}{[M_1] + r'_2[M_2]} = 1 - P'_{22} \quad (25)$$

Figure 5a,b shows the triad populations which were calculated by using eqs 20−25. Figure 6a,b shows the probabilities σ_{MM} and σ_{SM} which were estimated by substituting the populations F_{MMM} and F_{MSM} and the peak areas S_D and S_X in eqs 14 and 15, respectively. The values of σ_{MM} and σ_{SM} changed with composition in the copolymer.

Origin of Chirality in Polymer 4. As shown in Figure 6a, the σ_{MM} value decreases with an increase in the M_1 mole fraction. The extrapolated value of σ_{MM} to the M_1 fraction of 1.0 agrees very closely with the P_m value of 0.29 in PMMA derived from the homopolymerization of monomer **1**, where P_m is the probability of forming the meso diad and is estimated by the expression $P_m = (m) = (mm) + 0.5\,(mr)$. The tactic triad fractions (mm), (mr), and (rr) in PMMA derived from **1** are shown in Table 5 along with the data previously reported for PMMAs from the analogous monomers **5**,[23] **6**,[24] **7**,[25] and **8**[26] during cyclopolymerization. The polymerizations of **5**−**7** are indicated to follow Bernoulli behavior, but those of **1** and **8** are like the first-order Markov model. It is characteristic of PMMA derived from **1** that the fraction of tactic triad rr is significantly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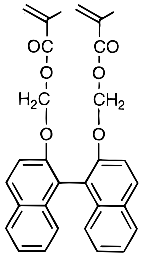
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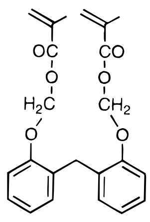
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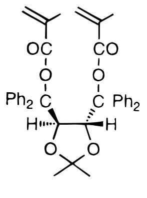
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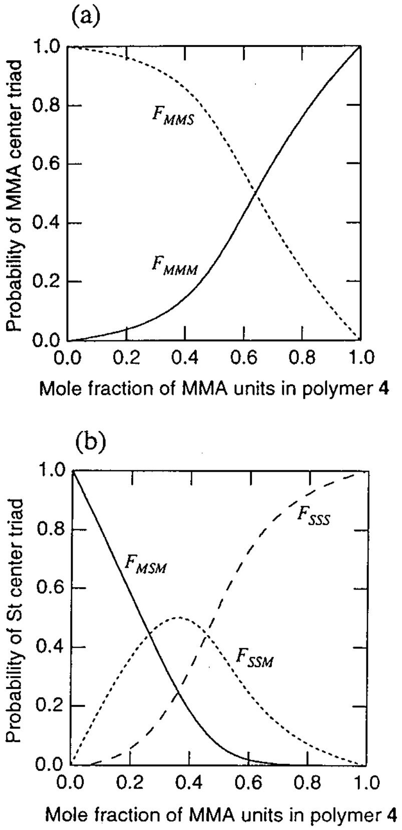


Figure 5. Populations of (a) MMA center triads and (b) St center triads calculated by using the reactivity ratios, $r_1' = 0.35$ and $r_2' = 0.36$, versus mole fraction of MMA units in polymer **4**.

high in contrast to the extremely high fraction of tactic triad *mm* in PMMA from **8**.

The probability σ_{MM} composed of σ'_{MM} and σ''_{MM} is due to the intramolecular cyclization in the M_1 unit and the intermolecular reaction in the M_1M_1 unit. The contribution of the latter to the formation of the diad sequence MM in polymer **4** increases with increasing fraction of the M unit and will be asymptotic to 0.5 in PMMA. The decrease in σ_{MM} with increasing M unit, therefore, implies $\sigma'_{MM} > \sigma''_{MM}$. The probability of forming the racemo diad MM is larger in the intermolecular reaction than in the intramolecular cyclization.

The chiroptical property of the copolymer after cleavage of the template becomes most active in the maximum fraction of the isolated M_1 unit, as indicated in previous papers.[4,7,8,14] When the M_2 unit is present as a spacer, the diad sequence derived from the M_1 unit exhibits chirality, resulting from the chiral racemo configuration. On the contrary, polymer **4** was more active in chirality with increasing M_1 unit, but nevertheless, PMMA from **1** was inactive. Although PMMA from **1** is peculiar in the high fraction of tactic triad *rr*, the comonomer unit as a spacer needs to convert the racemo sequence to a chiral chain. In addition to the racemo diad unit due to the isolated M_1 unit, the tetrad unit also becomes chiral when the intermolecular reaction forms the M_1M_1 unit with a racemo configuration, as shown in Scheme 2. The tactic tetrads *mrm*, *mrr*, and *rrr* are chiral, in spite of the configuration of the comonomer unit in both sides.

In the system of monomer **1**-St with $r'_1 = 0.35$ and $r'_2 = 0.36$, the number-average sequence length n_1 of the M_1 unit increases from 1.04 for the M_1 mole fraction of 0.1 in the feed to 1.82 and 2.40 for those of 0.7 and 0.8, respectively. Consequently, the chirality in polymer **4** should originate from the M tetrad sequence due to the M_1M_1 diad unit. Optically active PMMA was obtained from monomer **5**, the chirality of which was originally assigned to the tactic tetrad *mrr*.[23] The PMMAs produced through the cyclopolymerization differed from one another in tacticity according to the used template, as in Table 5. Such a change in tacticity must also be found in the cyclocopolymerization, thus having a direct effect on the behavior of chirality occurrence.

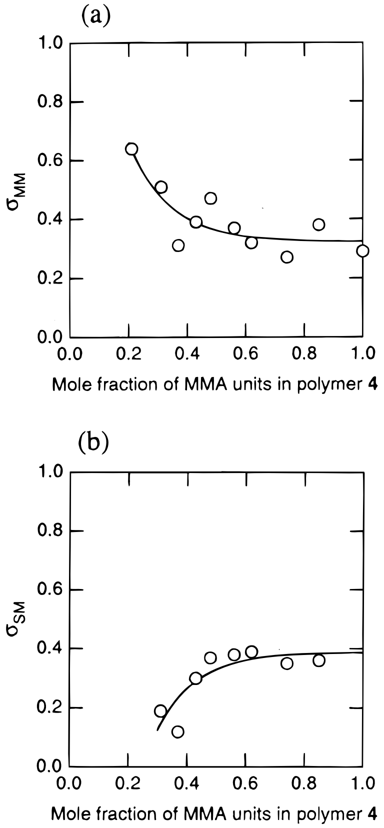


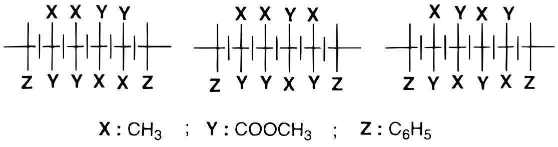
Figure 6. Probabilities (a) σ_{MM} and (b) σ_{SM} estimated by using eqs 14 and 15 versus mole fraction of MMA units in polymer **4**.

Table 5. Stereochemistry of Poly(methy methacrylate)s Derived from Radical Cyclopolymerizations of 1,2:5,6-Di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol (1) and the Analogous Monomers

	triad tactic fraction				
monomer	(*mm*)	(*mr*)	(*rr*)	P_m[a]	remark
1	0.20	0.18	0.62	0.29	this work
5	0.12	0.49	0.39	0.37	T. Kakuchi[b]
6	0.14	0.51	0.36	0.39	T. Nakano[c]
7	0.20	0.52	0.28	0.46	H. Guéniffey[d]
8	0.84	0.10	0.06	0.89	T. Nakano[e]

[a] Calculated by use of the expression $P_m = (mm) + 0.5(mr)$. [b] Data from ref 24. [c] Data from ref 25. [d] Data from ref 26. [e] Data from ref 27.

Scheme 2



In polymer **4**, the origin of chirality is assigned to the chiral tetrad sequences which are induced by participation of the considerably higher probability of forming the racemo diad through the intermolecular reaction in copolymerization.

Summary

Optically active poly(methyl methacrylate-*co*-styrene) was synthesized through the cyclocopolymerization of 1,2:5,6-di-*O*-isopropylidene-3,4-di-*O*-methacryloyl-D-mannitol (M_1) with styrene (M_2). The origin of chirality was discussed in comparison with the other cyclocopolymerization system. The following results were deduced and concluded.

(i) The monomer exhibited an extent of cyclization of 0.86 or above, which was only slightly influenced by incorporation of the comonomer.

(ii) The polymer after hydrolysis, poly(methyl methacrylate-*co*-styrene), was optically active, and the absolute value of its specific rotation increased with increasing mole fraction of M_1 units in the feed.

(iii) The 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 M_1M_1 in the copolymer.

(iv) The origin of chirality was assigned to the chiral tetrad MMA sequences. The occurrence behavior of chirality changed according to the template used.

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