Chirality Induction in Cyclopolymerization XVI. Synthesis of Optically Active Poly(methyl acrylate-co-dimethyl fumarate) by Radical Cyclopolymerization of Asymmetrical Nonconjugated Diene Having Chiral Pentanediol[†]

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(Received August 27, 2001; Accepted October 11, 2001)

ABSTRACT: The molecular design and synthesis of asymmetric bifunctional monomers, 3-(S)-acryloyloxy-1-(*S*)-methyl-butyl methyl fumarate (**1a**) and 3-(R)-acryloyloxy-1-(*R*)-methyl-butyl methyl fumarate (**1b**), have been carried out in terms of a novel method of producing optically active polymers based on cyclopolymerization. The polymerization of **1** proceeded *via* the cyclopolymerization mechanism to yield the cyclopolymer **2** with the extent cyclization of 0.87-0.96 when the monomer concentration ([*M*]) in the feed was $0.3 \mod L^{-1}$ or less. The number-average molecular weight (M_n) decreased with a decrease in the [*M*] from 8300 to 3300 for polymer **2a** and from 4200 to 2400 for polymer **2b**. The specific rotation ([α]²³₄₃₅, *c* 1.0, CHCl₃) of the resulting polymers changed from +19.3° to +33.4° for **2a** and from -26.2° to -34.9° for **2b**. In order to confirm the chirality induction, the chiral pentanediyl moiety was removed from polymer **2** by saponification, and the hydrolyzed polymer was treated with diazomethane to give poly(methyl acrylate-*co*-dimethyl fumarate) (**3**). The M_n was 2200–2600 for **3a** and 2300–5700 for **3b**, and the template-free polymers showed an optical activity with a specific rotation that ranged from -1.4° to -9.3° for **3a** and from +7.5° to +8.8° for **3b**. The CD spectra of **3a** showed a positive Cotton effect whereas **3b** showed a negative Cotton effect which is the mirror image of **3a**. The optical activity of polymer **3** should be attributed to the threo-erythro sequence of the methyl acrylate and dimethyl fumarate units.

KEY WORDS Cyclopolymerization / Chirality Induction / Chiral Template / Methyl Acrylate / Dimethyl Fumarate / Threo-Erythro Sequence / Enantioselective Cyclization /

In recent years, much research has been conducted on the synthesis of optically active vinyl polymers from the viewpoint of the fine control of the polymer main chain stereochemistry.^{1–3} Natta *et al.* reported the pioneering synthesis of optically active vinyl polymers by the polymerizations of a cyclic olefin or a conjugated diene, in which the cyclic unit and double bond in the main chain break down the symmetric property due to its repeating structure.⁴ In addition, cyclopolymerization is also a promising method to introduce a cyclic unit into the polymer, so that various types of asymmetric synthesis cyclopolymerizations, such as the enantioselective cyclopolymerizations of 1,5-hexadiene⁵ and benzaldehyde divinylacetal⁶ were realized.

Another way to destroy the symmetry of the vinyl polymer is the use of a second repeating unit. Wulff *et al.* realized the synthesis of configurationally chiral vinyl polymers through the cyclocopolymerization of D-mannitol bis(4-vinylborate) with achiral vinyl monomers.⁷ Furthermore, in our continuing studies on

the cyclocopolymerization of bis(4-vinylbenzoate)s of the chiral diol with styrene leading to poly[(methyl 4-vinylbenzoate)-*co*-styrene], we clarified the chiral main-chain configuration of the template free polymer using CD spectroscopy based on the exciton chirality method.⁸ In addition, because the optical rotation of the template-free polymer increased with an increase in the styrene unit in the polymer, an achiral monomer plays an important role in producing the optical activity of the template-free polymer. For this method using a divinyl monomer having a chiral template, an additional achiral monomer is essential to break down the symmetric property of the polymer main-chain.

Here, we would like to present a new way to break down the symmetric property of the polymer mainchain through the cyclo-homopolymerization of a bifunctional monomer having vinyl and vinylene groups. In this study, the asymmetric cyclopolymerizations of (R)-3-acryloyloxy-(R)-1-methyl-butyl methyl fumarate (1a) and its ennatiomer, *i.e.*, (S)-3-acryloyloxy-(S)-1methyl-butyl methyl fumarate (1b), were examined.

[†]This paper is dedicated to Professor Kazuaki Yokota on the occasion of his happy retirement.

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(i) AIBN, toluene, 60°C. (ii) KOH-MeOH, 18-crown-6. (iii) Diazomethane, ether-THF

Scheme 1.

After removal of the chiral template by saponification, the optical activity of the template-free polymer was estimated by an optical rotation measurement and CD spectroscopy. The main chain chirality was discussed on the basis of the infinite chain model and cyclopolymerization method.

EXPERIMENTAL

Measurements

The ¹H and ¹³C NMR spectra were recorded using JEOL JNM-EX-270 and JNM-A400II instruments. The molecular weights of the resulting polymers were measured by gel permeation chromatography (GPC) at 40°C in tetrahydrofuran (1.0 mL min⁻¹) using a Jasco GPC-900 system equipped with a Waters Ultrastyragel 7 µm column (linear, 7.8 mm × 300 mm) and two Shodex KF-804L columns (linear, 8 mm × 300 mm). The number-average molecular weight (M_n) was calculated on the basis of polystyrene calibration. The optical rotations were determined with a Jasco DIP-1000 digital polarimeter. The CD spectra were recorded at 21°C in hexafluoroisopropyl alcohol (HFIP) with a 5 mm path length using a Jasco J-720 spectropolarimeter.

Materials

Acryloyl chloride, 1,3-dicyclohexylcarbodiimide (DCC) 4-dimethylaminopyridine, fumaric acid, (2R,4R)-2,4-pentanediol, (2S,4S)-2,4-pentanediol, and dry toluene were purchased from Kanto Chemical Co. Inc. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Kanto Chemical Co. Inc. and recrystallized from methanol. Dichloromethane and *N*-methylpyroridone (NMP) were distilled over CaH₂. HFIP was donated from the Central Glass Co. and used without further purification. The seamless cellulose tube (UC24-32-100) was purchased from the Viskase Sales Co.

(R)-3-Hydroxy-(R)-1-methyl-butyl Methyl Fumarate (4a)

To a solution of (2R,4R)-2,4-pentanediol (12.5 g, methyl hydrogen fumarate⁹ 120 mmol), (10.4 g, 80 mmol) 4-dimethylaminopyridine and (0.8 g, 6.4 mmol) in CH₂Cl₂ was added a solution of DCC (18.2 g, 88 mmol) in CH_2Cl_2 (5 mL) at 5°C within 5 min. After stirring for 3 h at room temperature, the reaction mixture was washed with 0.5 N HCl and saturated NaHCO₃. The product was roughly purified by flash column chromatography on silica gel (Kiesel Gel 60) with CH_2Cl_2 /ethyl acetate (4/1) to give a crude product 4a, which was used in the next reaction without further purification. Yield, 10.8 g (62.7%).

(R)-3-Acryloyloxy-(R)-1-methyl-butyl Methyl Fumarate (1a)

To a solution of 4a (5.0 g, 23.1 mmol) in NMP (50 mL), acryloyl chloride (2.5 g, 27.5 mmol) was gradually added at 0°C. After stirring for 3 h at room temperature, the reaction mixture was diluted with water (50 mL) and then extracted with three portions of ether (50 mL). The combined extracts were washed with 5 wt% aqueous NaOH and water, then dried over Na₂SO₄. After the solvent was distilled off, the crude product was purified by flash column chromatography on silica gel (Kiesel Gel 60) with hexane/diethyl ether (7/3) to give **1a** as a colorless liquid. Yield, 2.0 g (32.7%). $[\alpha]_{435}^{23} = -162.8^{\circ}, [\alpha]_D^{23} = -79.0^{\circ} (c \ 1.0, CHCl_3)$. ¹H NMR (400 MHz, CDCl_3): δ (ppm) = 6.82 (s, 2 H, -CH = CH -), 6.39 (d, ³J_{trans} = 17.3 Hz, 1H, =CH₂), 6.07 (dd, ³J_{trans} = 17.4 Hz, ³J_{cis} = 10.4 Hz, 1H, =CH-), 5.81 (d, ³J_{cis} = 10.5 Hz, 1H, =CH₂), 5.12–5.03 (m, 2H, OCH), 3.81 (s, 3H, OCH₃), 1.89 (t, ³J = 6.5 Hz, 2H, $-CH_2 -$), 1.29 (t, ³J = 6.1 Hz, 6H, $-CH_3$). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.5 (*C*=O), 165.3 (*C*=O), 164.2 (*C*=O), 133.9 (-C=C-), 130.6 (-CH=), 128.5 (=CH₂), 68.6 (CH), 67.3 (CH), 52.2 (OCH₃), 42.0 (CH₂), 20.3 (CH₃). Anal. Calcd for C₁₃H₁₈O₆ (270.28): C, 57.77; H, 6.71. Found: C, 57.68; H, 6.69.

(S)-3-Hydroxy-(S)-1-methyl-butyl Methyl Fumarate (4b)

The procedure for **4a** was applied to the reaction of (2S,4S)-2,4-pentanediol (12.5 g, 120 mmol), methyl hydrogen fumarate (10.4 g, 80 mmol), 4-dimethylaminopyridine (0.8 g, 6.4 mmol), and DCC (18.2 g, 88 mmol) to give crude **4b**, which was used in the next reaction without further purification. Yield, 11.3 g (65.5%).

(S)-3-Acryloyloxy-(S)-1-methyl-butyl Methyl Fumarate (1b)

The procedure for 1a was applied to the reaction of 4b (3 g, 13.9 mmol) and acryloyl chloride (1.5 g, 16.5 mmol) to give 1b as a colorless liquid. Yield, 2.0 g (52.7%). $[\alpha]_{435}^{23} = +163.3^{\circ}, \ [\alpha]_D^{23} = +79.3^{\circ} \ (c \ 1.0,$ CHCl₃). ¹H NMR (400 MHz, CDCl₃): δ (ppm)=6.83 (s, 2H, -CH=CH-), 6.38 (d, ${}^{3}J_{\text{trans}} = 17.3 \text{ Hz}$, 1H, =CH₂), 6.07 (dd, ${}^{3}J_{\text{trans}} = 17.3 \text{ Hz}$, ${}^{3}J_{\text{cis}} = 10.5 \text{ Hz}$, 1H, =CH-), 5.81 (d, ${}^{3}J_{cis}$ = 10.5 Hz, 1H, =CH₂), 5.12-5.03 (m, 2H, OCH), 3.81 (s, 3H, OCH₃), 1.88 (t, ${}^{3}J = 6.5$ Hz, 2H, $-CH_{2}$ -), 1.29 (t, ${}^{3}J = 6.1$ Hz, 6H, $-CH_3$). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 165.5 (C=O), 165.4 (C=O), 164.3 (C=O), 134.0 (-C=C-), 133.1 (-C=C-), 130.6 (-CH=), 128.6 (=CH₂), 68.7 (CH), 67.4 (CH), 52.2 (OCH₃), 42.1 (-CH₂-), 20.3 (-CH₃). Anal. Calcd for C₁₃H₁₈O₆ (270.28): C, 57.77; H, 6.71. Found: C, 57.85; H, 6.70.

Polymerization of Monomer 1

The polymerizations were performed in a dried glass ampoule under a nitrogen atmosphere. Typical procedure is as follows: A solution of **1a** (0.51 g, 1.85 mmol) and AIBN (61.0 mg, 0.37 mmol) in toluene (18.5 mL) was degassed and backfilled three times with N₂. The polymerization was initiated by heating to 60° C in a water bath. After the appropriate time, the polymerization mixture poured into hexane and the precipitate was filtered. The obtained white powder was purified by reprecipitation with chloroform-hexane and dried *in vacuo*. Yield, 0.41 g (79.3%).

Synthesis of Template-Free Polymer 3

A typical procedure is as follows: To a solution of polymer 2 (300 mg) in THF (5 mL) in a Teflon[®] bottle was added 25 wt% methanolic KOH (9.35 g, 0.17 mol, 50 equiv. to the C=O groups in polymer 2) and 18-crown-6 (130 mg, 0.5 mmol, 0.15 equiv. to the C=O groups in polymer 2). The reaction mixture was refluxed for 50 h with the addition of sufficient water. After cooling, the mixture was neutralized by adding hydrochloric acid. The mixture was then placed in a cellulose tube and dialyzed for 2 days with distilled water. The aqueous solution in the cellulose tube was freezedried to yield a hydrolyzed polymer.

To a solution of the obtained polymer in THF was added a solution of diazomethane (*ca.* 0.5 M) in ether (350 mL). After stirring for 1 week at room temperature, the mixture was concentrated and dissolved in methanol. The methanol solution was diluted with water and then dialyzed using a cellulose tube for 2 days with distilled water. The aqueous solution in a cellulose tube was freeze-dried to give **3** as a white powder. Yield, 223.8 mg (90.6%).

RESULTS AND DISCUSSION

Cyclopolymerization

Asymmetric nonconjugated dienes **1a** and **1b** were synthesized according to the procedure represented in Scheme 2. Methyl hydrogen fumarate was reacted with enantiomerically pure templates, (2R,4R)and (2S,4S)-2,4-pentanediol, using DCC to yield (*R*)-3-hydroxy-(*R*)-1-methyl-butyl methyl fumarate (**4a**)



(i) (2R,4R)-2,4-pentanediol, DCC, CH₂Cl₂ (ii) (2S,4S)-2,4-pentanediol, DCC, CH₂Cl₂ (iii) acryloyl chloride, NMP

Scheme 2.

		Polymer 2						Polymer 3 ^f		
Run No.	Monomer	$\frac{[M]_0}{\operatorname{mol} \operatorname{L}^{-1}}$	$\frac{\text{Yield}}{\%^{\text{b}}}$	$M_{\rm n}(M_{\rm w}/M_{\rm n})^{\rm c}$	f_{c}^{d}	$[\alpha]_{435}^{e}$	Yield %	$M_{\rm n}(M_{\rm w}/M_{\rm n})^{\rm c}$	$[\alpha]_{435}^{e}$	
1	1a	0.5	-	gel	_	_	_	5700 (2.2)	-1.4°	
2		0.4	_	gel	-	-	-	2900 (3.1)	-6.7°	
3		0.3	97	8300 (13.1)	0.87	+19.5°	86	2900 (2.3)	-8.9°	
4		0.2	98	5700 (3.8)	0.91	+25.7°	98	3000 (1.6)	-8.4°	
5		0.1	79	3300 (1.8)	0.95	+33.4°	91	2300 (1.4)	-9.3°	
6	1b	0.2	88	4200 (2.0)	0.93	-26.2°	79	2600 (1.5)	+7.5°	
7		0.1	82	2400 (1.8)	0.96	-34.9°	70	2200 (1.3)	+8.9°	

Table I. Radical cyclopolymerizations of monomers 1a and 1b and synthesis of poly(methyl acrylate-co-dimethyl fumarate) (3)^a

^a1a, (*R*)-3-acryloyloxy-(*R*)-1-methylbutyl methyl fumarate; 1b, (*S*)-3-acryloyloxy-(*S*)-1-methylbutyl methyl fumarate; solvent, toluene; initiator, AIBN; temp., 60°C; [AIBN]₀ = 20 mmol L⁻¹. ^bHexane insoluble part. ^cDetermined by GPC using polystyrene standards. ^dExtent of cyclization determined by ¹H NMR spectra. ^cMeasured in CHCl₃ at 23°C (*c* 1.0). ^fPrepared from the hydrolysis of polymer **2** using KOH in aqueous MeOH, followed by the treatment with diazomethane.

and (*S*)-3-hydroxy-(*S*)-1-methyl-butyl methyl fumarate (**4b**), respectively. The reaction of **4a** and **4b** with acryloyl chloride in NMP afforded (*R*)-3-acryloyloxy-(*R*)-1-methyl-butyl methyl fumarate (**1a**) ($[\alpha]_{435}^{23} = -162.8^{\circ}$, *c* 1.0, CHCl₃) and (*S*)-3-acryloyloxy-(*R*)-1-methyl-butyl methyl fumarate (**1b**) ($[\alpha]_{435}^{23} = +163.3^{\circ}$, *c* 1.0, CHCl₃), respectively, as colorless liquids.

The radical polymerizations of **1a** and **1b** were carried out using AIBN in dry toluene at 60°C under a nitrogen atmosphere (Table I). For the monomer concentration $([M]_0)$ of $0.4 \text{ mol } \text{L}^{-1}$ and above, the polymerization of **1a** proceeded heterogeneously to yield an insoluble gel in common organic solvents. On the other hand, the polymerizations of **1a** and **1b** for the $[M]_0$ of $0.3 \text{ mol } \text{L}^{-1}$ and below proceeded homogeneously, and the resulting polymers were soluble in chloroform and tetrahydrofuran. The number-average molecular weight (M_n) decreased with the decreasing [M] in both polymers **2a** and **2b**.

In the ¹H NMR spectrum of the polymer obtained from 1a (Figure 1a), the signals at 5.8, 6.1, and 6.4 ppm due to the acryloyl group completely disappeared whereas the signal at 6.8 ppm due to the fumarate group was slightly observed. In addition, the obtained polymer was soluble in common organic solvents, when the monomer concentration was equal or less than 0.3 mol L^{-1} . This indicates that crosslinking is not very significant at least under this condition. Therefore, the radical polymerization of 1 proceeded through a cyclopolymerization mechanism to form the polymer consisting of 9- and 10-membered cyclic constitutional units with a small amount of residual fumarate group. Unfortunately, it was difficult to experimentally determine the predominant ring structures. The extent of cyclization (f_c) was estimated by the ratio of the signals due to the vinyl proton for the residual fumarate groups to the methine proton (4.6-5.5 ppm) of the pentanediyl



Figure 1. ¹H NMR spectra of monomer **1b** (a), polymer **2a** $([M]_0 = 0.1 \text{ mol } L^{-1})$ (b), and polymer **3a** $([M]_0 = 0.1 \text{ mol } L^{-1})$ (c).



Figure 2. CD spectra of polymers 2a and 2b.

groups in the ¹H NMR spectrum of polymer **2**. The f_c values increased with the decreasing $[M]_0$ in both polymers **2a** and **2b**.

Chiroptical Property of Polymers 2 and 3

The specific rotation ($[\alpha]_{435}^{23}$, c 1.0, CHCl₃) of polymer **2** changed from +19.3° to +33.4° for **2a** and from -26.2° to -34.9° for **2b**. Figure 2 shows the CD spectra of polymers **2a** and **2b**. Polymer **2a** shows a negative Cotton effect around 200–240 nm which is the exact mirror image of **2b**.

In order to confirm the chirality induction, the removal of the pentanediyl template from polymer **2** was carried out using methanolic potassium hydroxide with 18-crown-6 followed by methyl esterification with diazomethane. Figure 1 shows the ¹H NMR spectra of **2a** and its methylated polymer. The chiral template was completely removed from **2a**, because the signals at 4.6–5.5 ppm due to the methine proton in the chiral template completely disappeared. Thus, the methylated polymer corresponded to poly(methyl acrylate*co*-dimethyl fumarate) (**3**). Table I lists the results of the synthesis and characterization of polymer **3**. The M_n was 2200–2600 for **3a** and 2300–5700 for **3b**.

Polymer **3** showed an optical activity with a specific rotation ($[\alpha]_{435}$, *c* 1.0, CHCl₃) ranging from -1.4° to -9.3° for **3a** and from $+7.5^{\circ}$ to $+8.8^{\circ}$ for **3b**. Because the chiral template was completely removed, the optical activity is attributable to the main chain structure. Figure 3 shows the CD spectra of polymers **3a** and **3b**. The CD spectra of polymers **3a** and **3b**. The CD spectra of polymers **3a** and **3b** are the mirror image of each other, in which polymer **3a** shows a positive Cotton effect around 200–240 nm. These chiroptical properties suggest that the chiral template induces a new chirality in the main chain during the cyclopolymerization.

When the monomer concentration was 0.5 and



Figure 3. CD spectra of polymers 3a and 3b.



Figure 4. FT-IR spectra of monomer **1a** (a), polymer **2a-I** ($[M]_0 = 0.3 \mod L^{-1}$) (b), polymer **2a-II** ($[M]_0 = 0.4 \mod L^{-1}$) (c), and polymer **2a-III** ($[M]_0 = 0.5 \mod L^{-1}$) (d).

0.4 mol L⁻¹ (runs 1 and 2, respectively), the polymerization of **1a** gave a crosslinked polymer. The polymers **3a** and **3b** synthesized from these gels also show optical activity. The specific rotation ($[\alpha]_{435}$, *c* 0.1, CHCl₃) of polymer **3a** decrease from -8.9° to -1.4° with the increase in $[M]_0$ from 0.3 to 0.5 mol L⁻¹. This could be due to the change in cyclization extent, which is reduced by the intramolecular addition prior to cyclization. Figure 4 shows the IR spectra of monomer **1a** (a) and polymers **2a** which were synthesized under the condition of $[M]_0 = 0.3$ (b), 0.4 (c), and 0.5 mol L⁻¹ (d). The absorptions at 810 and 672 cm⁻¹ are assigned



to the C=C bond stretch in the acrylate and fumarate groups, respectively. For $[M]_0 = 0.3$, these two absorptions almost disappeared, which agreed with the ¹H NMR spectrum. The absorption due to the acrylate group dose not change very much among these polymers. However, the absorption due to fumarate dramatically increase with an increase in $[M]_0$. Although the unreacted fumarate group could be consumed as a closslink, this result indicates that the extent of cyclization decreased with an increase in $[M]_0$. Hence, the cyclization process is essential for inducing the chirality into the main chain.

Origin of Configurational Main-Chain Chirality

There are three possible constitutional sequences in polymer 3, i.e., erythro-erythro, threo-erythro, and threo-threo, without regard to the 9- or 10-membered cyclic unit in polymer 2 (Scheme 3, their enantiomers are omitted here). It is well known that the radical polymerization of dialkyl fumarate proceeded through *meso*-addition,¹⁰ so that two constitutional structures, i.e., erythro-erythro and threo-erythro, should be dominant. Taking into account the infinite chain model, the symmetric property of these sequences could be represented as square models. The square model of the erythro-erythro sequence possesses a symmetry plane, whereas that of the threo-erythro sequence is asymmetric. Hence, the optical activity in poly(methyl acrylateco-dimethyl fumarate) (3) should be attributed to the threo-erythro sequence, which is derived through the

enantioselective cyclization due to the chiral pentanediyl template.

CONCLUSION

We have demonstrated the synthesis of the optically active vinyl polymer through the cyclopolymerization of the monomer having a chiral template without any achiral comonomer. The radical polymerization of 3-(S)-acryloyloxy-1-(S)-methyl-butyl methyl fumarate (1a) and 3-(R)-acryloyloxy-1-(R)-methyl-butyl methyl fumarate (1b) proceeded through the cyclopolymerization mechanism. After removal of the chiral pentanediyl units from the cyclopolymers, the pentanediylfree polymer, poly(methyl acrylate-co-dimethyl fumarate), exhibited optical activity. For the chirality induction, the pentanediyl template in the monomers transmitted its chirality to the main chain of the pentanediyl-free polymer through the intramolecu-In addition, the optical activity in lar cyclization. poly(methyl acrylate-co-dimethyl fumarate) should be attributed to the threo-erythro sequence, which is derived through the enantioselective cyclization due to the chiral template.

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