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Chirality induction in cyclocopolymerization. 15. Enhancement of chirality induction during cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) with styrene using alkylaluminum compounds

T. Kakuchi[a,*], M. Tsuji[a], A. Narumi[a], H.-O. Shimomura[b], M. Obata[b], K. Yokota[b]

[a]*Division of Bioscience, Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060-0810, Japan*
[b]*Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan*

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Abstract

The cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) (**1**) with styrene was carried out in dry toluene at 40°C in the presence of triethylaluminum (Et_3Al), diethylaluminum chloride (Et_2AlCl), and ethylaluminum dichloride ($EtAlCl_2$), which played the role of Lewis acid capable of coordinating on carboxyl groups. After removal of the (2*S*,3*S*)-2,3-butanediyl units, the template-free polymer **3** exhibited an optical activity due to its main chain chirality. The specific rotations ($[\alpha]_{435}$, *c* 1.0, $CHCl_3$) of polymers **3** prepared with alkylaluminum compound varied from −11.2 to −21.7°, which was higher than those prepared without alkylaluminum compound (−9.0°). The specific rotation of polymer **3** increased with an increase in the acidity of the alkylaluminum compounds (i.e. $Et_3Al < Et_2AlCl < EtAlCl_2$) and/or with an increase in the molar ratio of alkylaluminum compound to monomer **1**. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Chirality induction; Cyclocopolymerization; Alkylaluminum compound

1. Introduction

The cyclocopolymerization of the divinyl monomer having a chiral template with the monovinyl comonomer is a certain method for producing an optically active polymer whose chirality is due to configurational asymmetry [1]. We have reported that the cyclocopolymerization of bis(4-vinylbenzoate) of a chiral diol with styrene gave the optically active poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**) [2]. The optical activity is attributable to the enantiomeric racemo diad, i.e. the (*R*,*R*)- and (*S*,*S*)-racemo diad, formed through the cyclization of bis(4-vinylbenzoate). In addition, we proposed a mechanism for chirality induction in the polymerization on the basis of the results of the radical cyclization experiment and its computational study [3]. From the radical cyclization experiment, the chirality induction was found mainly in the intermolecular addition of the cyclized radical. Furthermore, the computational study suggested that the chirality induction was driven by the chiral orientation of two carboxyl groups, which affects the stability of the cyclized radical. Hence, the chiral control for the conformation of two carboxyl groups seems to be one of the important functions of the chiral template.

One of the promising methods of conformational control of a carboxyl group is the addition of Lewis acid capable of coordinating to a carbonyl group. For example, Sibi and Ji [4] demonstrated chemo- and stereoselectivity enhancement in the radical cyclization of *N*-enoyloxazolidinones by means of the manipulation of the rotamer population in substrates using Lewis acid such as tri-*n*-butyltin chloride. Nishida et al. [5] reported that Lewis acid promoted diastereoselective radical cyclization. They showed that Lewis acid such as triethylaluminum (Et_3Al) and methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) improved diastereoselectivity in the cyclization of (−)-8-phenylmenthyl (*E*)-2-nonen-8-ynoate. Hence, Lewis acid capable of coordinating to a carbonyl group should serve as a modifier of chirality induction owing to steric crowding of the coordinating Lewis acid.

In this paper, we report the asymmetric cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) (**1**)

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* Corresponding author. Tel./fax: +81-11-706-2255.
E-mail address: kakuchi@ees.hokudai.ac.jp (T. Kakuchi).

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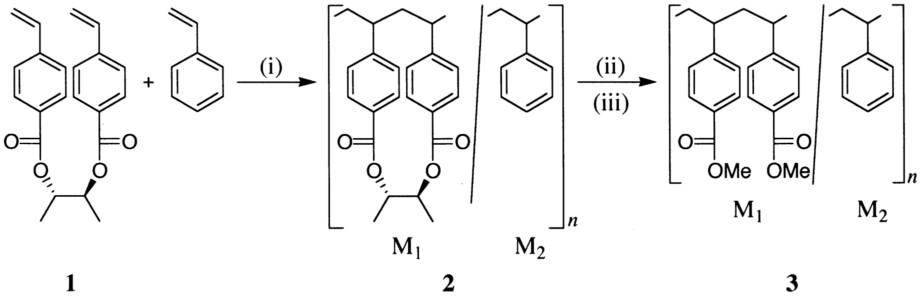

Scheme 1.

with styrene in the absence and the presence of alkylaluminum compounds (Scheme 1). In order to confirm the chirality induction, the chiral template was removed from the resulting polymer, followed by treatment with diazomethane to yield poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**). The effect of the alkylaluminum compound was discussed on the basis of the chiroptical property of polymer **3**.

2. Experimental

2.1. Materials

Dry toluene was purchased from Kanto Chemical Co. and used without further purification. 2,2′-Azobis(2-methylpropionitrile) (AIBN) was recrystallized from methanol. Ethylaluminum dichloride ($EtAlCl_2$) and diethylaluminum chloride (Et_2AlCl) were purchased as hexane solution (0.93 and 0.95 mol l^{-1}, respectively) from Kanto Chemical Co. Et_3Al in hexane (1.1 mol l^{-1}) was purchased from Tokyo Chemical Industry Co. HFIP was donated by Central Glass Co. and used without further purification. (2*S*,3*S*)-2,3-Butanediyl bis(4-vinylbenzoate) (**1**) was synthesized according to a previous paper [6].

2.2. Cyclocopolymerization

Divinylmonomer **1**, styrene, and AIBN were taken in a round-bottom flask and dissolved in dry toluene. After degassing this solution, a predetermined amount of organoaluminum compound was added. Polymerizations were carried out at 40°C in a thermostated shaker. After an appropriate time, the polymerization mixture was poured into methanol. After removal of an aluminum compound by washing with methanol containing aqueous 4 M HCl (50 vol.%), the precipitate was filtered. The obtained white powder was purified by reprecipitation with chloroform–methanol and dried in vacuo.

Table 1
Cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) (**1**, M_1) with styrene (M_2) in the presence of alkylaluminum compounds

Polymer **2**[a]								Polymer **3**[b]		
Additive	[Al]/[**1**][c]	Time (h)	Yield (%)	f_1[d]	f_c[d]	M_n (M_w/M_n)[e]	$[\alpha]_{435}$[f] (°)	Yield (%)	M_n (M_w/M_n)[e]	$[\alpha]_{435}$[f] (°)
None	–	42	9	0.29	0.93	10 300 (1.67)	+ 245	54	7000 (1.68)	−9.0
	–[g]	44	18	0.28	0.91	2300 (1.86)	+ 226	46	2300 (1.70)	−9.0
Et_3Al	1	64	21	0.25	0.98	4700 (2.03)	+ 226	38	3700 (2.16)	−11.2
	2	22	22	0.30	0.89	3400 (2.32)	+ 212	40	3400 (2.24)	−12.8
	3	15	15	0.31	0.86	3000 (2.16)	+ 216	46	2900 (2.15)	−14.0
Et_2AlCl	1	64	16	0.26	0.90	6000 (2.15)	+ 241	42	4900 (2.05)	−12.5
	2	49	22	0.30	0.95	3800 (2.96)	+ 262	44	4400 (2.18)	−16.5
	3	24	27	0.30	0.97	3100 (2.64)	+ 269	47	2400 (2.44)	−18.9
$EtAlCl_2$	1	72	18	0.25	0.97	7200 (2.59)	+ 214	45	5900 (2.95)	−15.3
	2	58	18	0.33	0.99	6900 (3.02)	+ 221	43	7900 (1.98)	−18.6
	3	34	28	0.32	0.95	3200 (3.82)	+ 255	35	2300 (2.64)	−21.7

[a] Solvent, toluene; initiator, AIBN (1 g l^{-1}); temperature, 40°C; [**1** + styrene] = 0.1 mol l^{-1}; mole fraction of **1** in the feed, 0.1.

[b] Prepared from polymer **2**.

[c] Molar ratio of alkylaluminum compound to monomer.

[d] Mole fraction of M_1 unit in the polymer (f_1) and extent of cyclization (f_c) were determined by quantitative ^{13}C NMR spectra.

[e] Determined by GPC using a polystyrene standard.

[f] Measured in $CHCl_3$ at 23°C (*c* 1.0 g dl^{-1}).

[g] Ten times as much AIBN (10 g l^{-1}) as in the usual cases was added.

*2.3. Synthesis of poly[(methyl 4-vinylbenzoate)-co-styrene] (**3**)*

The removal of the chiral template from polymer **2** was carried out using methanolic KOH. After neutralization with hydrochloric acid, the solution was dialyzed using a cellophane tube and concentrated by freeze-drying. The hydrolyzed copolymer was treated with diazomethane in ether/benzene to give poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**).

2.4. Measurements

^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-EX270 and JNM-A400II instruments. Quantitative ^{13}C NMR spectra were obtained at 30°C in $CDCl_3$ (100 mg ml^{-1} delay time 7.0 s; inverse gated decoupling). FT-IR spectra were recorded using the Perkin–Elmer 1600 Series (16 scans, resolution 4.0 cm^{-1}, NaCl cell, and cell length 1 mm). The molecular weight of the resulting polymers was measured by gel permeation chromatography (GPC) in tetrahydrofuran on a Jasco Intelligent HPLC system (880-PU pump and 830-RI Detector) equipped with three polystyrene columns (Shodex KF-804L). The number-average molecular weight (M_n) was calculated on the basis of a polystyrene calibration. Optical rotations were measured with a Jasco DIP-140 digital polarimeter. CD spectra were measured at 24°C in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with a 0.5 cm path length using Jasco J-720 spectropolarimeter.

3. Results

3.1. Cyclocopolymerization

Table 1 lists the results of the cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) (**1**) with styrene using AIBN in toluene at 40°C in the presence of Et_3Al, Et_2AlCl, and $EtAlCl_2$. Without the alkylaluminum compounds, the polymerization systems were homogeneous and the resulting polymer **2** was soluble in chloroform and tetrahydrofuran. On the other hand, the polymerizations in the presence of the alkylaluminum compound proceeded heterogeneously. After the removal of the alkylaluminum compound, however, polymers **2** were soluble in common organic solvents such as chloroform and tetrahydrofuran. Hence, the formation of the insoluble part during polymerization was caused not by gelation, but by chelation with the alkylaluminum compounds. When the amount of alkylaluminum compound increased, the polymerization rate increased and the number-average molecular weights (M_ns) of polymers **2** decreased. The acceleration of polymerization should cause an increase in the decomposition rate of AIBN by the coordination of the aluminum compound [7]. In addition, the increase of radical concentration leads to the decrease in M_n of the polymer. In order to clarify the effect of the M_n value on the chiroptical property of polymer **3**, the polymerization using 10 times the amount of AIBN (10 g l^{-1}) was carried out to yield polymer **2** having the minimum value of M_n in Table 1. The composition (f_1) and the extent of cyclization (f_c) of polymer **2** were within the narrow range from 0.25 to 0.33 for f_1 and from 0.86 to 0.99 for f_c.

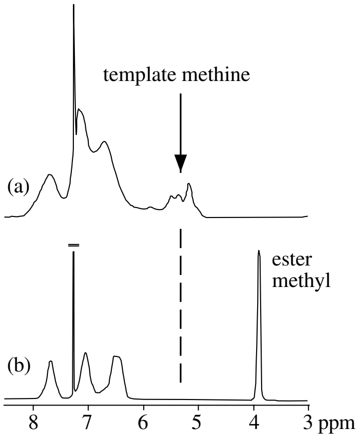

Fig. 1. ^{1}H NMR spectra of: (a) polymer **2** ($[EtAlCl_2]/[\mathbf{1}] = 3$); and (b) polymer **3** in $CDCl_3$ at 24°C.

3.2. Template-free polymers

In order to confirm the chirality induction, it is necessary to remove quantitatively the chiral templates from polymer **2**. The removal of the chiral template from polymer **2** was carried out using KOH in aqueous MeOH, and then the hydrolyzed polymer was treated with diazomethane to give polymer **3**. The absence of the template in the resulting polymer **3** was confirmed by the disappearance of the absorption at 3.6–5.2 ppm due to the template in the ^{1}H NMR spectrum (Fig. 1). The results of the hydrolysis and methyl esterification of polymer **2** were listed in Table 1. All polymers **3** showed optical activity even after removal of the chiral template so that the new chirality was introduced into the polymer main chain. Polymers **3** prepared without alkylaluminum compound showed the specific rotation of −9° regardless of the M_n value, indicating that the chiroptical

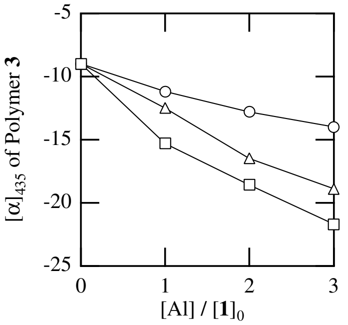

Fig. 2. Specific rotations of polymers **3** as a function of the molar ratio of alkylaluminum compound to monomer **1**.

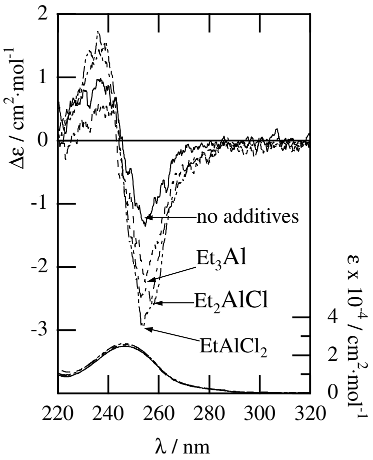

Fig. 3. CD (upper) and UV (lower) spectra of polymers **3** ([Al]/[**1**] = 3). The $\Delta\varepsilon$ and ε values are based on the concentration of the methyl benzoate diad unit.

property of polymer **3** was not affected by M_n in the range of 2300–7000. Polymer **3** prepared with alkylaluminum compounds have a larger specific rotation than that prepared without additives, as listed in Table 1. This result indicates that alkylaluminum compounds enhanced the chirality induction into the main chain. Fig. 2 shows the specific rotation of polymer **3** as a function of the molar ratio of alkylaluminum compound to monomer **1** ([Al]/[**1**]). Using the same alkylaluminum compound, the specific rotation of polymer **3** increased with an increasing [Al]/[**1**] value. For the same [Al]/[**1**], the specific rotation of polymer **3** increased with an increase in the order of $Et_3Al < Et_2AlCl < EtAlCl_2$. The enhancement of optical activity was also confirmed by the CD spectra of polymer **3** (Fig. 3). The sign of split Cotton effect of polymer **3** indicates that these polymers consist of a higher content of the (*R*,*R*)-racemo benzoate diad than of the (*S*,*S*)-racemo, which is the same as the chiroptical result reported [6]. The amplitude of split Cotton effect, i.e. the *A* value, increased in the same order for the specific rotation, indicating that the enhancement of optical activity is attributable to the promotion of the preferential formation of the (*R*,*R*)-racemo structure in the cyclic unit.

4. Discussion

The optical activity of polymer **3** increased in the order of $Et_3Al < Et_2AlCl < EtAlCl_2$ and with an increase in the [Al]/[**1**] value as shown in Fig. 2. The order of the alkylaluminum compounds coincides with the order of the Lewis acidity which can be confirmed by IR spectroscopy. Fig. 4 shows the IR spectra of monomers **1** with and without alkylaluminum compounds. In the case without the alkylaluminum compound, the stretching vibration of the C=O double bond of monomer **1** appeared at 1721 cm^{-1} in the IR spectra. This absorption shifted toward the lower wave number with the addition of the alkylaluminum compound and the shift ($\Delta\nu_{C=O}$) increased in the order of $Et_3Al < Et_2AlCl < EtAlCl_2$. Hence, the results indicate that the specific rotation of polymer **3** increased with an increase of the net amount of the coordinating Lewis acid. The chirality induction ability is affected by the surroundings around the carboxylate groups, and the alkylaluminum compound promoted chirality induction by coordinating on to the carboxyl groups in monomer **1**. In other words, the monomer **1** coordinated with alkylaluminum compound has a higher ability of chirality induction than the free monomer **1**.

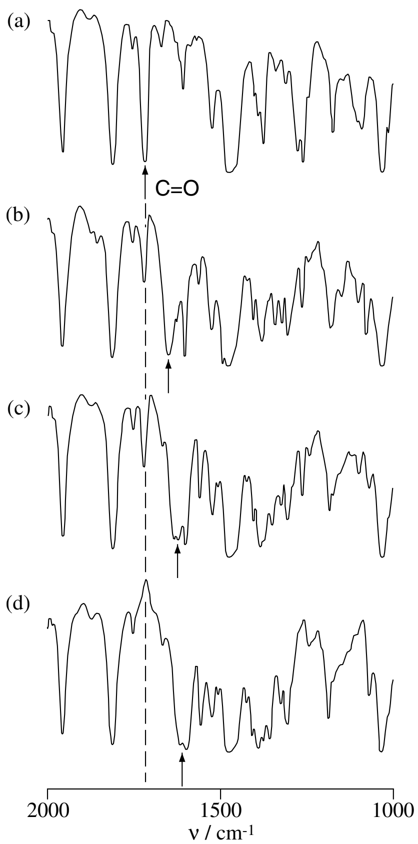

Fig. 4. IR spectra of: (a) monomer **1**; (b) monomer **1** with Et_3Al; (c) Et_2AlCl; and (d) $EtAlCl_2$ in benzene solution ([**1**] = 0.1 mol l^{-1}, [Al]/[**1**] = 3, ambient temperature under argon).

The model for chirality induction, which is supported by semiempirical molecular orbital calculation, suggested that the carboxylate groups in monomer **1** play an important role in chirality induction [3]. According to the model, the stereoselection during the intermolecular addition of the cyclized radical was controlled by the chiral orientation of two carboxylate groups (Fig. 5). The cyclized radical, in which the *Si* face for the carboxylate groups is directed toward the inside (conformer **A**), inhibits the formation of the cyclic unit having (*S*,*S*)-racemo configuration, resulting in the preferential formation of the (*R*,*R*)-racemo diad rather than the (*S*,*S*)-racemo. Here, the chiral orientation of the two carboxyl groups was caused by steric crowding around the chiral alcoholic residue of benzoate and intramolecular

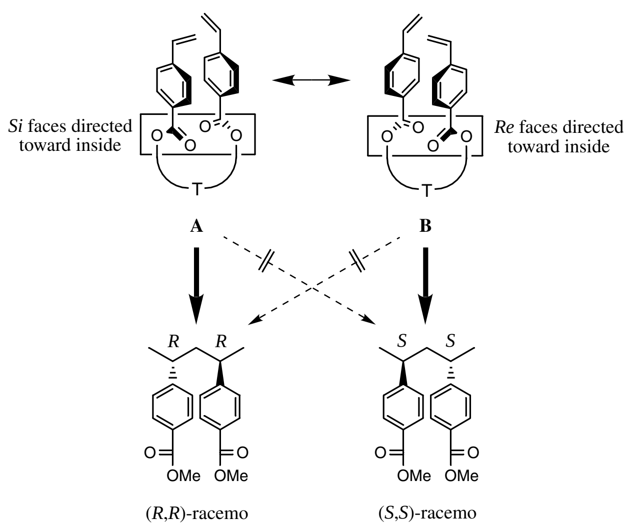

Fig. 5. Enantiomorphic conformations of carboxyl groups.

dipole–dipole interaction between the two carbonylate groups. Alkylaluminum compounds cause an increase in the bulkiness and polarizability of the carbonyl groups to indicate the difference between the two enantiomorphic carboxylate orientations (Fig. 6), resulting in the enhancement of chirality induction into the main chain.

5. Conclusions

The optical activity of poly[(methyl 4-vinylbenzoate)-*co*-styrene] (**3**), which was prepared through the cyclocopolymerization of (2*S*,3*S*)-2,3-butanediyl bis(4-vinylbenzoate) with styrene, increased with the addition of alkylaluminum compounds into the polymerization media. The higher the acidity of the alkylaluminum compounds used and/or the higher the molar ratio of additives to monomer applied, the larger was the optical acidity of polymer **3** shown. This effect can be explained as a result of the promotion of chiral orientation control in carboxyl groups by means of the coordination of alkylaluminum compound. The result supports the chirality induction mechanism reported previously.

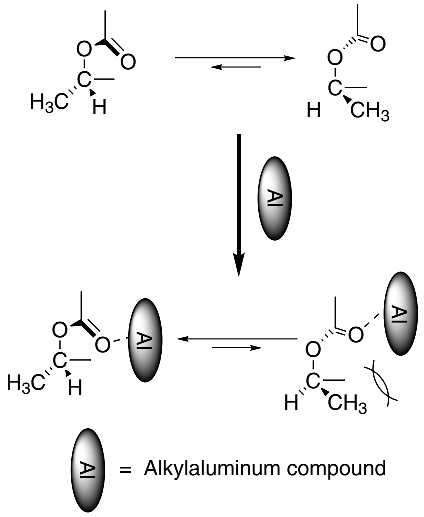

Fig. 6. Effects of alkylaluminum compound on the conformations of carboxylate groups.

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