Macromolecules **2003,** *36,* 7055−7064

Threo-Disyndiotactic Polymerization of (*E*,*E*)-Alkyl Sorbates Assisted by Bulky Organoaluminum Lewis Acid via "Alternating Turning over Polymerization (ATOP)" Mechanism

Akinori Takasu,* Masaya Ishii, Yoshihito Inai, and Tadamichi Hirabayashi

Department of Environmental Technology and Urban Planning, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Katsuhiro Inomata

Department of Materials Science and Engineering, School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Received April 8, 2003; Revised Manuscript Received July 8, 2003

ABSTRACT: *(E,E)*-Methyl sorbate (MS) and *(E,E)*-ethyl sorbate (ES), i.e., methyl 2,4-hexadienoate and ethyl 2,4-hexadienoate, underwent anionic polymerization in toluene at −60 to 0 °C in the presence of organoaluminum Lewis acids. The NMR, wide-angle X-ray diffraction (WAXD), and semiempirical molecular orbital calculation demonstrated that 1,4-trans-threo-disyndiotactc polymerization occurred (tritactic polymerization). Coordination of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD) (MAD/*t*-BuLi = 3) played three important roles, stabilization of the propagating anion, the activation of the monomer, and dissociation of *tert*-butyllithium (*t*-BuLi) aggregated in toluene to give polymers with relatively narrow molecular weight distribution (M_w/M_n = 1.3) using *t*-BuLi−(−)-menthyl ethyl ether (MEE) complex as the initiator. Hydrogenations of poly(MS) and poly(ES) with *p*-toluenesulfonylhydrazide (TSH) produced head-to-head (H−H) poly(propylene-*alt*-methyl acrylate) and poly(propylene-*alt*-ethyl acrylate), respectively, which enabled us to evaluate the stereochemistry including diastereoselectivity and stereoregularity of poly(alkyl sorbate)s in detail. The polymer from *t*-BuLi-MEE/MAD initiator system (at −60 °C) showed the highest stereospecificity, i.e., threo(99%)-disyndiotacticity(95%). The glass transition temperature of the threo poly(MS) is 27 °C with melting endotherm at 102 °C. The thermal property depends on the stereochemistry. Furthermore, we indicate that the polymerization proceed via "alternating turning over polymerization (ATOP)" mechanism, in which Lewis acid coordinated monomers are inserted into the propagating center with alternating turning over.

Introduction

The polymerization of dienes can proceed in a variety of ways depending on the chemical structure of the dienes. Dienes are classified as conjugated or nonconjugated dienes, which is defined by whether the two double bonds are conjugated with each other or not. In contrast to recent progress in controlling of the structure of vinyl polymers,[1] that in the control of structure of conjugated diene polymers including molecular weight, regioselectivity (chemoselectivity), stereochemistry (geometry, diastereoselectivity, and stereoregurality) is not enough. In particular, the stereoregularity is hard to control due to the inability of controlling the propagating step. However, physical properties of diolefine polymers are often influenced by the polymeric stereoregularity.[2] We have already investigated regioselective (1,4-addtion) anionic polymerizations of polar diene monomers, i.e., methyl 2-methyl-2,4-hexadienoate (MMHd) and methyl 2,4-dimethyl-2,4-pentadienoate (MDMPd),[3] and reported that subsequent hydrogenation of the polymers affords head-to-head (H−H) and head-to-tail (H−T) poly(propylene-*alt*-methyl methacrylate)s, respectively, as the first synthesis of poly(propylene-*alt*-methyl methacrylate).[4] This article reports a new stereospecific polymerization of sorbic acid derivatives assisted by bulky aluminum Lewis acid and the polymerization mechanism, although we have already reported threo diastereoselective polymerization as a preliminary communication.[5] 1,4-Disubstituted dienes generate two adjacent chiral centers during the propagation step.[6] Therefore, diastereoselectivity is essential for stereospecific polymerization for sorbic acid derivatives.

Shown in Figure 1, four different stereoregular polymers are possible for a trans-1,4-polymer (erythro-diisotactic, erythro-disyndiotactic, threo-diisotactic, and threo-disyndiotactic).[6] Sorbic acid derivatives were polymerized by anionic,[7] radical,[8] group-transfer,[9] and topochemical (crystalline state)[10] polymerizations. Natta et al.[7] have described anionic polymerization of alkyl sorbates, which produced highly stereoregular polymers with 1,4-trans-erythro-diisotactic structure (tritactic polymer, i.e., one geometric and two asymmetric centers) by a chiral initiator[7a] or a chiral additive.[7a,b] Matsumoto et al. discovered that crystalline-state polymerization of 1-naphthylmethylammonium salt of sorbic acid occurred stereospecifically to give the 1,4-trans-erythro-diisotactic polymer.[10] However, syntheses of the other three types of highly stereoregular polymers have not been reported.

This paper deals with the first threo-disyndiotactic polymerizations of sorbic acid derivatives, i.e., *(E,E)*-methyl sorbate (MS) and *(E,E)*-ethyl sorbate (ES), by anionic polymerization in an isotropic state (Scheme 1). Moreover we revealed that the polymerization proceed via "alternating turning over polymerization (ATOP)" mechanism, in which Lewis acid coordinated monomers are inserted into the propagating center with alternat-

---

* To whom correspondence should be addressed. E-mail: takasu.akinori@nitech.ac.jp.

10.1021/ma030211z CCC: $25.00

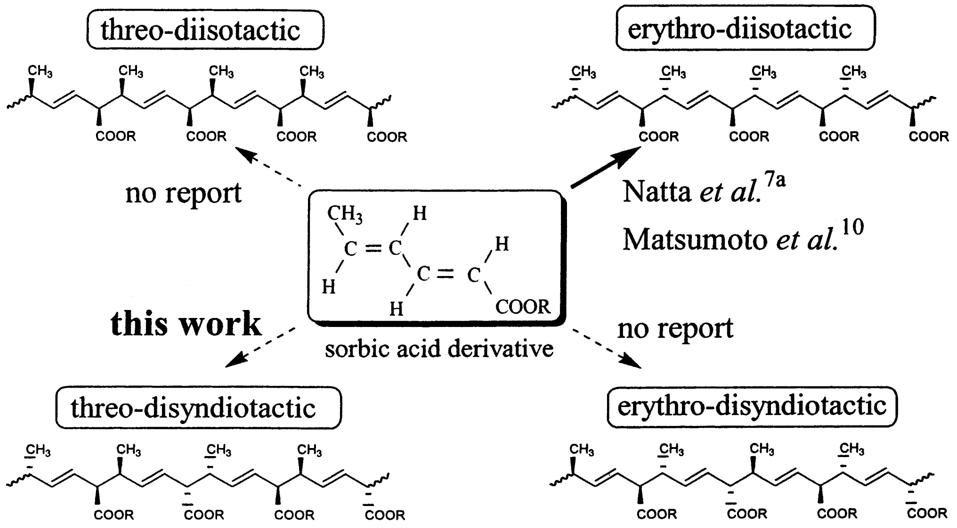
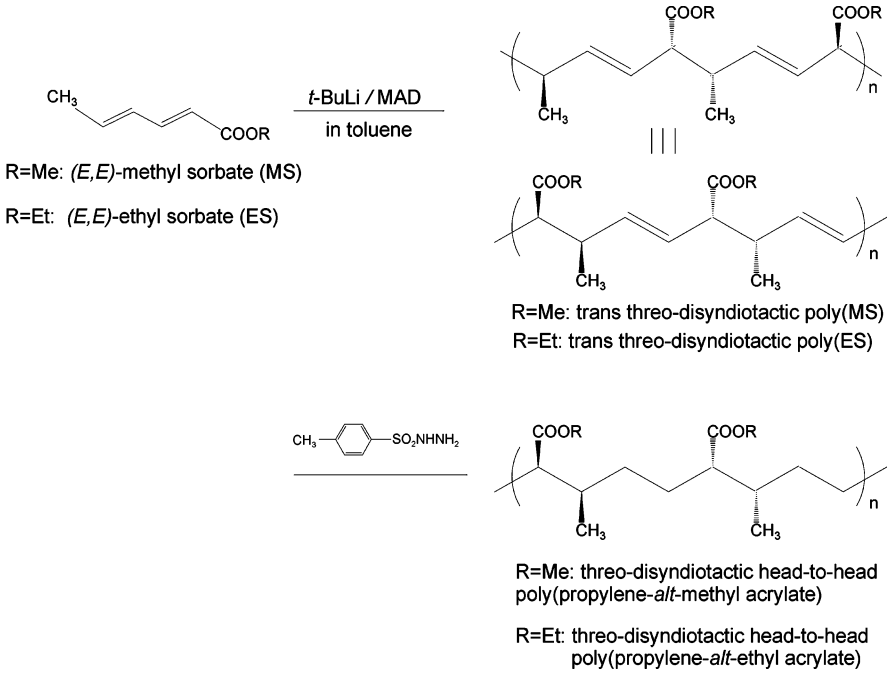


Figure 1. Four types of stereoregular (tritactic) poly(sorbic acid derivative)s.

Scheme 1. Threo-Disyndiotactic Anionic Polymerization of Alkyl Sorbates and Subsequent Hydrogenation



ing turning over. Any guide and control for the stereospecific polymerization of polar diene monomers in isotropic state would enable a wide range of new materials to be synthesized.

Experimental Section

Materials. MS (>97%) and ES (>98%) were obtained from Tokyo Kasei Co. (Tokyo, Japan). *tert*-Butyllithium (*t*-BuLi, 1.5 M *n*-pentane solution), and *p*-toluenesulfonylhydrazide (TSH, 95%) were purchased from Kanto Chemical Co., Inc. (Tokyo, Japan,) and used without further purification. Menthyl ethyl ether (MEE) was prepared by Williamson etherification from (−)-menthol (Tokyo Kasei Co., Tokyo, Japan, >99%) and ethyl iodide (Tokyo Kasei Co., Tokyo, Japan, >99%).

Anionic Polymerization of Alkyl Sorbates. In a typical anionic polymerization of MS, MS (1.01 g, 8.0 mmol), toluene (4.2 mL), and a toluene solution of methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD, 0.4 M, 1.2 mL, 0.48 mmol) were placed in an Schlenk tube equipped with a rubber septum under N_2. A solution of *t*-BuLi in *n*-pentane (1.5 M, 0.11 mL, 0.16 mmol) was added to the solution. After the tube was kept in a cooling bath at −20 °C for 72 h, reaction mixture was poured into methanol (500 mL) containing a trace amount of aqueous HCl. A white powder was isolated by repeated precipitation from chloroform into methanol. For poly(MS) (96% yield, run 4 in Table 1). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.96 ($-CH-CH_3$), 2.58 ($-CH\text{-}CH_3$), 2.81($-CH\text{-}CO-$), 3.65 ($-OCH_3$), 5.32−5.38 ($=CH-$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 17.6−18.7 ($-CH\text{-}CH_3$), 38.7−39.8 ($-CH-CH_3$), 51.6 ($-OCH_3$), 55.0 ($-CH-CO-$), 125.6−127.0 ($=CH-CH-CH_3$), 135.7−136.5 ($=CH-CH-CO-$), 173.6 ($-COOCH_3$). IR (KBr disk, cm^{-1}): 2843 (ν_{C-H}), 1735 [$\nu_{C=O}$(ester)], 1667 ($\nu_{C=C}$), 1435 (δ_{C-H}), 1254 and 1161 [ν_{C-O-C}(ester)], 971 ($\delta_{C=C-H}$). For poly(ES) (98% yield, run 4 in Table 2). ^1H NMR (400 MHz, $CDCl_3$, δ, ppm): 0.95 ($-CH-CH_3$), 1.20 ($-OCH_2CH_3$), 2.56 ($-CH-CH_3$), 2.73 ($-CH-CO-$), 4.10 ($-OCH_2CH_3$), 5.37 ($=CH-$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 14.2 ($-OCH_2CH_3$), 17.7−18.6 ($-CH-CH_3$), 38.8−39.5 ($-CH-CH_3$), 55.1−56.3 ($-CH-CO-$), 60.5 ($-OCH_2CH_3$), 125.6−127.0 ($=CH-CH-CH_3$), 135.9−136.5 ($=CH-CH-CO-$), 173.0 ($-COOCH_2CH_3$). IR (KBr disk, cm^{-1}): 2962 (ν_{C-H}), 1730 [$\nu_{C=O}$(ester)], 1683 ($\nu_{C=C}$), 1462 (δ_{C-H}), 1260 and 1174 [ν_{C-O-C}(ester)], 967 ($\delta_{C=C-H}$).

Hydrogenation of Poly(MS) and Poly(ES). A solution of poly(MS) and TSH in toluene was stirred at 110 °C for 72

Table 1. Anionic Polymerization of Methyl Sorbate (MS) in Toluene[a] and the Stereochemistry

entry	initiator	additive[b]	temp (°C)	yield (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c	T_g^d (°C)	T_m^d (°C)/ΔH (J/g)	hydrogenation[e] threo/erythro[f]	disyndio/diiso[f]
1	*t*-BuLi		−20	28	6.2	2.8$_7$	5	not detected	40/60	51/49 (threo)
2	*n*-BuLi-MEE[g]		−40	21	2.3	1.8$_9$	30	195/31	0/100	19/81 (erythro)
3	*t*-BuLi	MAD[h]	−20	98	5.4	1.4$_6$	18	not detected	92/8	57/48 (threo)
4	*t*-BuLi−Sp[i]	MAD[h]	−20	96	3.1	1.2$_3$	21	not detected	94/6	65/35 (threo)
5	*t*-BuLi	MAD[h]	−40	13	3.4	1.3$_0$			95/5	67/33 (threo)
6	*t*-BuLi−Sp[i]	MAD[h]	−40	79	3.1	1.3$_7$	20	not detected	97/3	72/28 (threo)
7	*t*-BuLi-MEE[g]	MAD[h]	−40	21	2.3	1.8$_9$	20	not detected	96/4	81/19 (threo)
8	*t*-BuLi−Sp[i]	MAD[h]	−50	98	4.2	1.6$_6$	23	96/13	95/5	83/17 (threo)
9	*t*-BuLi-MEE[g]	MAD[h]	−50	88	4.4	1.6$_3$	23	97/12	94/6	92/8 (threo)
10	*t*-BuLi−Sp[i]	MAD[h]	−60	87	3.3	1.4$_5$	27	104/20	94/6	92/8 (threo)
11	*t*-BuLi-MEE[g]	MAD[h]	−60	71	4.5	1.3$_8$	27	102/22	99/1	95/5 (threo)

[a] $[\mathrm{M}]_0 = 1.5$ mol/L; $[\mathrm{M}]_0/[\mathrm{I}]_0 = 50$; time, 72 (runs 1−9) and 168 h (runs 10 and 11). [b] Feed molar ratio of aluminum compound to initiator ($[\mathrm{Al}]_0/[\mathrm{I}]_0 = 3$). [c] Determined by SEC in THF relative to polystyrene. [d] Determined by DSC (heating rate: 10 °C/min). [e] [repeating unit]$_0$ = 0.14 mol/L in toluene at 110 °C for 72 h, [TSH]$_0$/[repeating unit]$_0$ = 3.0. Yields: 84−99%. [f] Determined by ^{13}C NMR measurement in $\mathrm{CDCl_3}$ after hydrogenation. [g] (−)-Menthyl ethyl ether. [h] Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [i] (−)-Sparteine.

Table 2. Anionic Polymerization of Ethyl Sorbate (ES) in Toluene[a] and the Stereochemistry

run	initiator	additive	$[\mathrm{Al}]_0/[\mathrm{I}]_0{}^b$	temp (°C)	yield (%)	$M_n^c \times 10^{-4}$	M_w/M_n^c	hydrogenation[d] yield (%)	threo/erythro[e]	disyndio/diiso[e]
1	*t*-BuLi		0	0	11	3.9	1.7$_8$	85	25/75	52/48 (threo)
2	*t*-BuLi−Sp[f]		0	−20	15	2.8	2.0$_5$	75	0/100	20/80 (erythro)
3	*t*-BuLi	MAD[g]	3	0	trace	-				
4	*t*-BuLi	MAD[g]	5	0	98	10.1	1.5$_2$	95	88/12	62/38 (threo)
5	*t*-BuLi	*i*-$\mathrm{Bu_3Al}$	5	0	0	-				
6	*t*-BuLi	MAD[g]	5	−20	86	7.4	1.4$_3$	86	94/6	87/13 (threo)
7	*t*-BuLi−Sp[f]	MAD[g]	5	−40	trace					
8	*t*-BuLi−Sp[f]	MAD[g]	5	−20	92	6.2	1.2$_7$	85	93/7	79/21 (threo)
9	*t*-BuLi-MEE[h]	MAD[g]	5	−20	96	6.4	1.1$_7$	86	92/8	93/7 (threo)

[a] For 72 h, $[\mathrm{M}]_0 = 1.5$ mol/L, $[\mathrm{M}]_0/[\mathrm{I}]_0 = 50$. [b] Feed molar ratio of aluminum compound to initiator. [c] Determined by SEC in THF relative to polystyrene. [d] [repeating unit]$_0$ = 0.14 mol/L in toluene at 110 °C for 72 h, [TSH]$_0$/[repeating unit]$_0$ = 3.0. [e] Determined by ^{13}C NMR measurement in $\mathrm{CDCl_3}$ after hydrogenation. [f] (−)-Sparteine. [g] Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [h] (−)-Menthyl ethyl ether.

h under $\mathrm{N_2}$. Hydrogenation of the poly(MS) led to head-to-head poly(propylene-*alt*-methyl acrylate). Experimental procedure was same as that for hydrogenation of poly(MMHd) or poly(MDMPd) in our previous report.[4] A solution of poly(MS) (0.55 g, 4.4 unit mmol) and *p*-toluenesulfonylhydrazide (2.44 g, 13.1 mmol) in toluene (28 mL) was stirred at 110 °C for 72 h under $\mathrm{N_2}$. The solvent was evaporated, and the polymeric material was purified by reprecipitation from chloroform into methanol, and dried in vacuo to yield white powder (0.54 g, 98% yield, run 6 in Table 1). For poly(propylene-*alt*-MA) (95% yield, run 6 in Table 1). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 0.81, 0.98 $(-\mathrm{CH}-\mathrm{C}H_3)$, 1.25 $(-\mathrm{C}H_2-\mathrm{CH}-\mathrm{CH_3})$, 1.39 $(-\mathrm{C}H_2-\mathrm{CH}-\mathrm{CO}-)$, 1.57 $(-\mathrm{C}H-\mathrm{CH_3})$, 2.14 $(-\mathrm{C}H\text{-}\mathrm{CO}-)$, 3.59 $(-\mathrm{OC}H_3)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 16.4−16.9 $(-\mathrm{CH}-C\mathrm{H_3})$, 25.8, 26.3 (erythro), 26.6, 26.8, 27.1, 27.3 (threo) $(-C\mathrm{H_2}-\mathrm{CH}-\mathrm{CO}-)$, 32.3, 32.4, 32.9 $(-C\mathrm{H_2}-\mathrm{CH}-\mathrm{CH_3})$ 35.3, 35.5, 35.8, 35.9 $(-C\mathrm{H}-\mathrm{CH_3})$, 50.6−50.9 $(-\mathrm{COO}C\mathrm{H_3})$, 51.1 (threo) $(-C\mathrm{H}-\mathrm{CO}-)$, 175.3, 175.6 (threo), 175.8, 175.9 (erythro) $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2924 ($\nu_{\mathrm{C-H}}$), 1734 [$\nu_{\mathrm{C=O}}$(ester)], 1457 ($\delta_{\mathrm{C-H}}$), 1166 [$\nu_{\mathrm{C-O-C}}$(ester)]. For head-to-head poly(propylene-*alt*-ethyl acrylate): (98% yield, run 4 in Table 2). ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, δ, ppm): 0.81, 0.98 $(-\mathrm{CH}-\mathrm{C}H_3)$, 1.25 $(-\mathrm{C}H_2-\mathrm{CH}-\mathrm{CH_3})$, 1.39 $(-\mathrm{C}H_2-\mathrm{CH}-\mathrm{CO}-)$, 1.57 $(-\mathrm{C}H-\mathrm{CH_3})$, 2.14 $(-\mathrm{C}H-\mathrm{CO}-)$, 3.59 $(-\mathrm{OC}H_3)$. ^{13}C NMR (100 MHz, $\mathrm{CDCl_3}$, δ, ppm): 14.2−14.3 $(-\mathrm{O}-\mathrm{CH_2}C\mathrm{H_3})$ 16.3−16.7 $(-\mathrm{CH}-C\mathrm{H_3})$, 26.0, 26.5 (erythro), 26.9, 27.0, 27.3, 27.4 (threo) $(-C\mathrm{H_2}-\mathrm{CH}-\mathrm{CO}-)$, 32.5 $(-C\mathrm{H_2}-\mathrm{CH}-\mathrm{CH_3})$ 35.1−35.7 $(-C\mathrm{H}-\mathrm{CH_3})$, 59.8 $(-\mathrm{COO}C\mathrm{H_2CH_3})$, 50.8, 50.9 (threo) $(-C\mathrm{H}-\mathrm{CO}-)$, 175.0, 175.1 (threo), 175.4 (erythro) $(-C\mathrm{OOCH_3})$. IR (KBr disk, cm^{-1}): 2962 ($\nu_{\mathrm{C-H}}$), 1730 [$\nu_{\mathrm{C=O}}$(ester)], 1456 ($\delta_{\mathrm{C-H}}$), 1174 [$\nu_{\mathrm{C-O-C}}$(ester)].

Semiempirical Molecular Orbital Calculation. A model, $\mathrm{CH_3-CH{=}CH-[CH(COOCH_3)-C(CH_3)-CH{=}CH]}_n\mathrm{-CH_3}$ (n = 10), was energy-minimized by the PM3 molecular orbital (MO) method[11] in MOPAC 2000 (MOPAC 2000 version 1.0, Fujitsu Ltd., Tokyo, Japan, 1999). The minimization was carried out with the variables of all bond length, bond angles, and torsion angles using the decamer having a S−G+S− trans S+G−S+ trans conformation for the starting conformation.

Measurements. FT IR spectra were recorded on a JASCO FT/IR-430 spectrometer in KBr disks. ^{1}H NMR spectra were measured at 27 °C using Bruker DPX-200 (200 MHz) or JEOL JNM-GX400 (400 MHz) spectrometers. ^{13}C NMR spectra (100 MHz) were measured on a Varian UNITY PLUS 400 spectrometer. All chemical shifts were expressed as δ downfield from tetramethylsilane (TMS). Number-average molecular weights (M_n) and the polydispersity indexes (M_w/M_n) of polymers were estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using system of Tosoh HLC 803D with a Tosoh RI-8020 detector and Tosoh G2000- (bead size, 5 μm; pore size, 60 Å), G3000- (bead size, 5 μm; pore size, 100 Å), G4000- (bead size, 5 μm; pore size, 200 Å), and G5000-HXL (bead size, 9 μm; pore size, 500 Å) columns (eluent, THF; flow rate, 1.0 mL/min; temperature, 40 °C). Differential scanning calorimetry (DSC) was measured on a DSC 210 unit with a Seiko SSC/5200H TA Station unit from −50 to +200 °C at a heating rate of 10 °C /min. The instrument was calibrated with an indium standard. A sample of 4−6 mg was used in an aluminum pan with a lid. The glass transition temperature (T_g) was determined at the inflection point of the corresponding heat capacity jump of the DSC trace. T_m and enthalpy of fusion were determined from the beginning and the area of the melting peak, respectively. CD and UV absorption spectra were simultaneously recorded using a JASCO J-600 spectrometer in acetonitrile solvents at 27 °C. The path length of the quartz cell was 1.0 mm, and the concentration was 0.5 mg/mL. These solvents were purified by distillation before use. Wide-angle X-ray diffraction (WAXD) patterns were taken by using flat-plate camera with Ni-filtered Cu Kα radiation (wavelength λ = 0.15405 nm) generated by a Rigaku Geigerflex at 40 kV and 20 mA. The camera length was calibrated with silicon. The uniaxially oriented sample was prepared by stretching the melt-quenched amorphous sample and subsequent annealing near the T_m.

Results and Discussion

1,4-Trans Regioselective Anionic Polymerization of Methyl Sorbate Catalyzed by Bulky Aluminum Lewis Acid. Anionic polymerizations of MS were carried out in toluene from −60 to 0 °C using *t*-BuLi as the initiator in the presence of organoaluminum regents. All of the resulting polymers were white solids and soluble in chloroform. It was confirmed by IR and ^{1}H and ^{13}C NMR measurements that MS polymerized with 100% 1,4-trans regioselectivity.[5] The ^{1}H NMR spectra showed that the resonances of the backbone methyl group were observed only at 0.96 ppm, characteristic of methyl group on a saturated carbon rather than vinylic carbon. This excluded the possibility of any 1,2- or 3,4-additions. The IR absorption of the residual double bond in the main chain was observed at 971 (δ_{C-H}) cm^{-1}, indicating trans geometry. ^{13}C NMR also supported complete 1,4-addition. Although Dorman et al. reported that the responses of carbons 1 and 4 in *cis*-2-hexene were shifted to 5.1−5.9 ppm high field of those of *trans*-2-hexene,[12] the proton-decoupled resonance signals of carbons were all single, differed by 1.4 ppm in the ^{13}C NMR spectrum. Hertler et al.[9] reported that Michael addition-type group-transfer polymerization of MS gave a polymer composed of cis (22%) and trans (78%) structure (the geometric structure was not regulated), in which methine carbons of $CHCH_3$ (40.34 and 40.54 ppm) and $CHCOOCH_3$ (55.71 and 56.46 ppm) in trans structure were distinguishable from those in the cis structure [$CHCH_3$ (35.48 ppm), $CHCOOCH_3$ (50.43 and 50.97 ppm)]. Poly(MS)s obtained in this study exhibited resonances at 38.7−39.8 ($-CH-CH_3$) and 54.8−55.4 ($-CH-COOCH_3$), and the peaks assigned to cis structure were not observed at all.

In the absence of an organoaluminum compound, the molecular weight and molecular weight distribution were difficult to control. The molecular weight of the poly(MS) ($M_n = 6.2 \times 10^4$) determined by SEC was higher than that calculated from the monomer/initiator ratio [M_n(calcd) $= 0.18 \times 10^4$], and the molecular weight distribution was broad ($M_w/M_n = 2.8_7$). The broad molecular weight distributions might be ascribed to attack of the polymer anion at the carbonyl group of the MS monomer. It was reported that polymerization of methyl methacrylate by *t*-BuLi/organoaluminum compound produces stereoregular poly(methyl methacrylate) with narrow molecular weight distributions in toluene.[13,14] We used similar initiator systems for the polymerization. For MS, it is considered that coordination of a Lewis acid to the carbonyl group should promote 1,4-trans-addition and simultaneously prevents the carbonyl attack on the ester group. In our previous study of anionic polymerization of methyl 2-methyl-2,4-hexadienoate (MMHd), we got the 1,4-trans polymer in the best yield, when the ratio of aluminum compound and initiator ($[Al]_0/[Li]_0$) was 3.[3,4] Therefore, we carried out the polymerization of MS at the same ratio ($[Al]_0/[Li]_0 = 3$). The coordinations of various bulky aluminum compounds with MS monomer were confirmed by ^{13}C NMR measurement in toluene-d_6. δ-Carbon (138.8 ppm) of MS monomer shifted toward lower field in the 1:1 mixture (mol/mol) of MS/aluminum compound, MS/triisobutylaluminum (i-Bu$_3$Al) (142.6 ppm), MS/methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[15] (145.1 ppm), MS/aluminum tris(2,6-diphenylphenoxide) (ATPH)[16] (141.2 ppm), and ethylaluminum bis(2,6-diphenylphenoxide) (EADP)[5] (141.5 ppm). Unexpectedly, MS was scarcely polymerized except for *t*-BuLi/MAD initiator systems.[5] Organoaluminum aryloxides are bulky but do not reduce the Lewis acidity much.[15] Aluminum phenoxide (MAD/*t*-BuLi = 3) played three important roles, (1) stabilization of the propagating anion (2) the activation of the monomer, and (3) dissociation[14] of *t*-BuLi aggregated in toluene, while alkyl aluminum cannot disrupt the aggregation of *t*-BuLi and living chain ends.[15] Also, the propagation took place selectively between the less reactive propagation anion and activated MS. Among the aluminum pheoxides, MAD was suitable for the polymerization to produce polymers with relatively narrow molecular weight distributions in an excellent yield ($M_n = 5.4 \times 10^4$, $M_w/M_n = 1.4_6$, run 3 in Table 1). It seemed that more bulky organoaluminum compounds, such as ATPH and EADP, suppressed the polymerization due to steric repulsion between bulky Lewis acid-coordinated MS and the propagating enolate.

Threo-Diastereoselectivity.[5] In the high-resolution (100 MHz) ^{13}C NMR spectrum of poly(MS) initiated by *t*-BuLi/−, splitting of the resonance assigned to $-COOCH_3$ is observed at 51.4 and 51.6 ppm, which ascribed to erythro and threo configurations, respectively, because the geometry in the double bond is confirmed to be all trans. In the spectrum of the polymer prepared by *t*-BuLi/MAD, only a sharp signal at 51.6 ppm was observed, indicating that anionic polymerization of MS assisted by MAD proceeds threo-diastereoselectively.[5] However, this ^{13}C NMR analysis did not allow us to quantify the ratio of erythro/threo structures because of overlapping of the peaks; i.e., their chemical shift difference ($\Delta\delta$) was very low (0.2 ppm). Hydrogenation of the internal double bonds made it possible to evaluate the stereochemistry in detail. This technique was effective in the study of the tacticities of 1,4-polydienes.[7d,17] The poly(MS)s were converted to the saturated polymers, i.e., H−H poly(propylene-*alt*-methyl acrylate)s by diimide generated by thermal decomposition of *p*-toluenesulfonylhydrazide (TSH)[4,5,18] (yield, 84−98%). The ^{13}C NMR spectrum of the hydrogenated poly(MS) prepared by *t*-BuLi/MAD at −20 °C is shown in Figure 2, together with those of hydrogenated poly(MS) from *t*-BuLi initiator and hydrogenated erythro-diisotactic poly(MS) prepared by anionic polymerization initiated by *n*-BuLi-MEE complex (run 2 in Table 1).[7b] The chemical shifts became to reflect their different diastereoselectivity clearly ($\Delta\delta$ value became higher), and the erythro/threo structure was distinguishable from the signals due to $-CH_2-$ (25.0−26.5 ppm for erythro and 26.6−27.6 ppm for threo, $\Delta\delta = 1.35$ ppm) and carbonyl carbons (175.8−176.2 ppm for erythro and 175.2−175.7 ppm for threo, $\Delta\delta = 0.55$ ppm). The erythro and threo ^{13}C NMR assignments were identified with those of poly(MS)s made by anionic[7] and group-transfer[9] polymerizations, and confirmed by a model compound, 5-methoxycarbonyl-2,6,9-trimethyldecane.[7d] As reported by Natta et al.,[7] the *t*-BuLi-MEE/− initiator system afforded poly(MS) with 100% of erythro diastereoselectivity at −40 °C (Figure 2c). In contrast, the ratio of threo/erythro of hydrogenated poly(MS) from *t*-BuLi/MAD system was 92/8 (Figure 2a) and that for poly(MS) from the *n*-BuLi/− system was 40/60 (Figure 2b). This is the first example of highly (>90%) threo-diastereoselectivie polymerization of a sorbic acid derivative that we know of.[5]

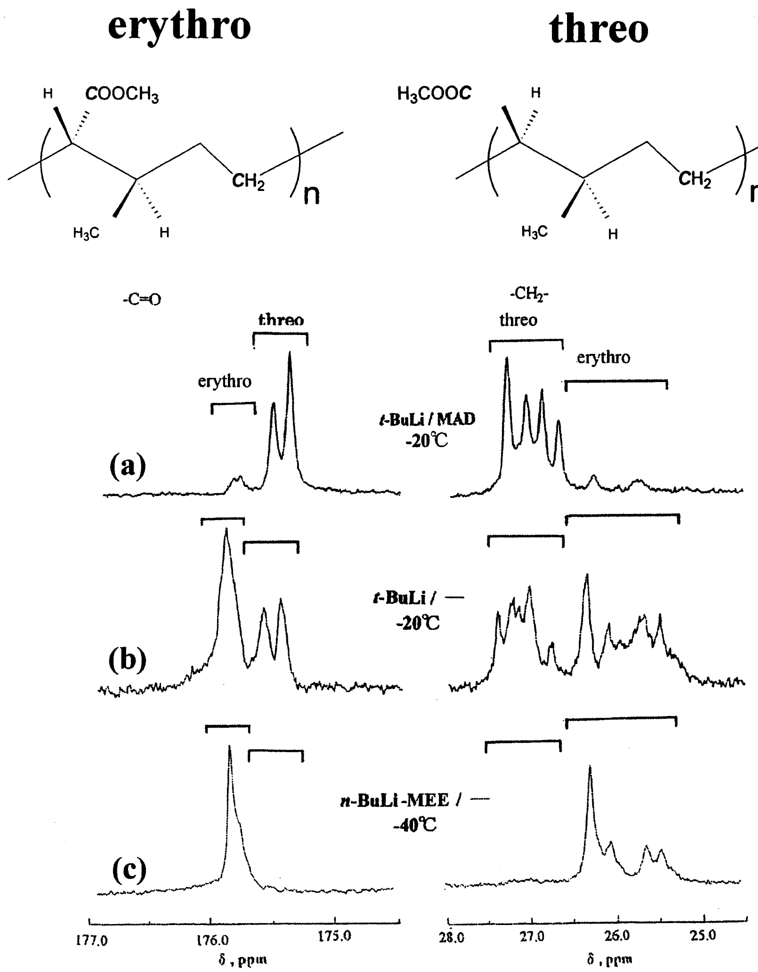


Figure 2. Expanded ^{13}C NMR spectra (in CDCl$_3$) of hydrogenated poly(MS)s, prepared by (a) *t*-BuLi/MAD, (b) *t*-BuLi/−, and (c) *n*-BuLi-MEE/− initiator systems.

We consider the erythro and threo structures generated by a propagating step (antiperiplanar transition state) as shown in Figure 3, in which we believe that conformation of the terminal MAD-coordinated MS dienolate is s-trans conformation predominantly. The significant predominance was supported by energy-minimization by a semiempirical molecular orbital method[11] using dimer model composed of terminal MAD-coordinated dienolate and penultimate units, which was due to apparent steric hindrance between the ester group in the penultimate unit and MAD-coordinated enolate. Therefore, we could exclude the possibility of the s-cis conformation. Therein, there is a greater number of nonbonded interactions in the threo adduct than in the erythro adduct in the absence of the Lewis acid (Figure 3, bottom). Provided that MS monomer and polymer anion are coordinated with MAD, there might be fewer unfavorable nonbonded interactions in the threo adduct because of remarkable steric repulsion between bulky MAD coordinated enolate and ester carbonyl of the inserted monomer (Figure 3, top). We consider this to be driving force of the higher threo diastereoselectivity.

t-BuLi/(−)-sparteine (Sp)[19] initiator (run 4) was effective for improving the molecular weight distribution (M_w/M_n = 1.2$_3$) as well as threo-diastereoselectivity (threo/erythro = 94/6) in the presence of MAD. MEE as well as Sp improved the threo-diastereoselectivity (run 7, 9, 11). Not only additives but also temperature affected the diastereoselectivity. *t*-BuLi-MEE/MAD ini-

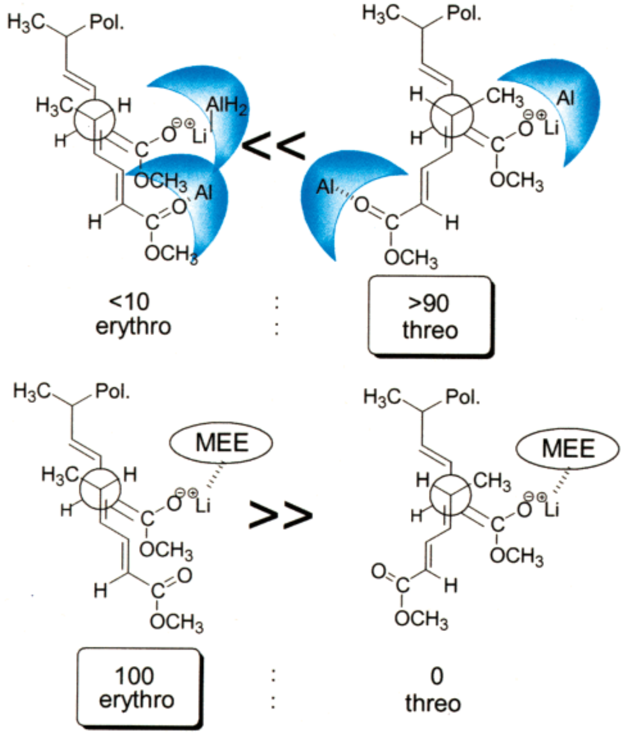


Figure 3. Antiperiplanar transition-state models for threo (top) and erythro (bottom) propagation in anionic polymerization.

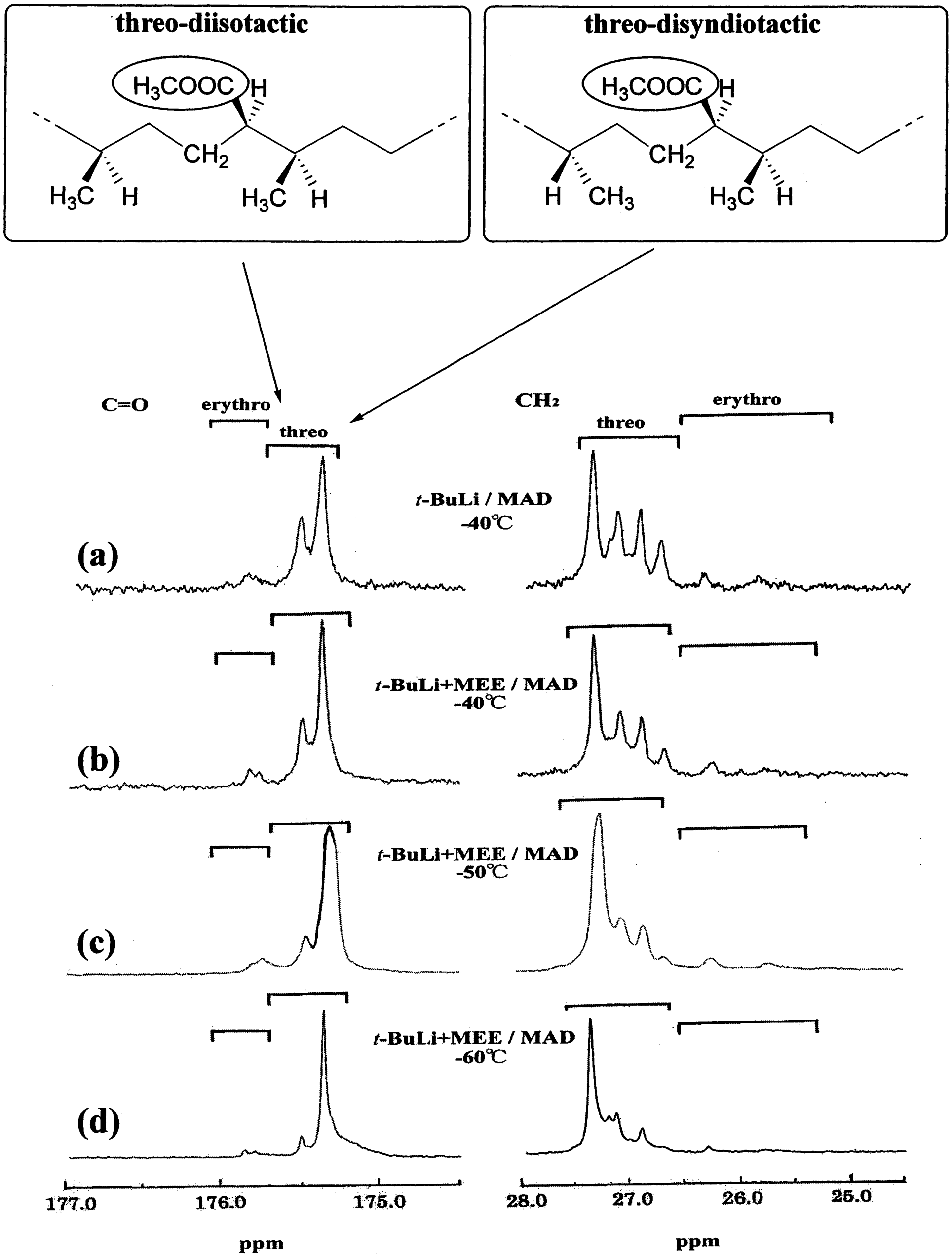


Figure 4. Expanded ^{13}C NMR spectra (in $CDCl_3$) of hydrogenated poly(MS)s, prepared by (a) *t*-BuLi/MAD (−40 °C), (b) *t*-BuLi-MEE/MAD (−40 °C), (c) *t*-BuLi-MEE/MAD (−50 °C), and (d) *t*-BuLi-MEE/MAD (−60 °C) initiator systems.

tiator system gave the highest threo diastereoselectivity (99%) at −60 °C (run 11 in Table 1, Figure 4d).

Disyndiotactic Stereoregularity. There are two types (diisotactic and disyndiotactic) of possible stereoregular structures for the *trans*-*threo*-1,4-polymer of poly(sorbic acid derivative)s (Figure 1, left).[6] The resonance of a threo carbonyl carbon of the hydrogenated poly(MS) was split into two peaks clearly at 175.3 and 175.6 ppm (Figure 4), which is assigned to the two stereoregularities. In the spectrum, the carbonyl carbon assigned to erythro structure was also split to two peaks (175.8 and 175.9 ppm). The intensity ratio of the peaks in the threo structure ($I_{175.3\ \mathrm{ppm}}/I_{175.6\ \mathrm{ppm}}$) increased from 51/49 (*t*-BuLi/−) to 57/43 (*t*-BuLi/MAD) at −20 °C. These results show that coordination of MAD improves the tacticity and threo diastereoselectivity. Chiral additive and temperature also influence on the stereoregularity. When the polymerization temperature was lowered to −40 °C, the $I_{175.3\ \mathrm{ppm}}/I_{175.6\ \mathrm{ppm}}$ value apparently increased to 67/33 in *t*-BuLi/MAD system (run 5 and Figure 4a). *t*-BuLi-MEE complex induced the higher stereoregularity in the presence of MAD at −40 °C (81/19, run 7 and Figure 4b) and the tacticity was much more improved in the polymerization at −50 °C (92/8, run 9 and Figure 4c) and at −60 °C (95/5, run 11 and Figure 4d). In the two stereoregular poly(MS)s, the threo-diisotactic polymer possesses optical activity, while the threo-disyndiotactic polymer was achiral because of the existence of a mirror glide plane.[6] In the CD measurement of poly(MS) obtained from *t*-BuLi-MEE/MAD system (run 11), we could not observe any clear Cotton effect (190−600 nm). As to the other carbons assigned to $-CH_2CH(COOCH_3)-$ which were observed at 26.6, 26.8, 27.1, and 27.3 ppm, they were also influenced by the tacticity. The intensities of two of them (27.1 and 27.3 ppm) increased with improvement of the stereoregularity and the other resonances might be ascribed not to the configuration but the conformation.

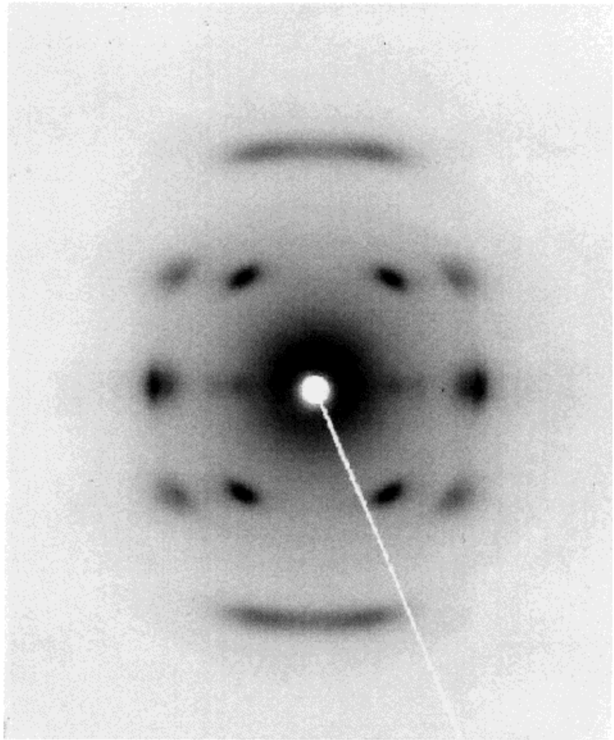


Figure 5. Wide-angle X-ray diffraction pattern of oriented film of threo(99%)-disyndiotactic(95%) poly(methyl sorbate) (run 14 in Table 1).

To evaluate the tacticity (diiso or disyndiotactic), WAXD measurements of the uniaxially oriented samples were carried out. WAXD pattern of poly(MS) prepared by *n*-BuLi-MEE is consistent with a 1,4-trans-erythro-diisotactic structure (fiber identity period c = 4.9 Å), which coincided with WAXD result reported by Farina et al. (c = 4.8 ± 0.1 Å).[7b] Corradini et al.[20] reported that threo-diisotactic poly(MS) having prevailingly threo configuration (threo 75%) has a chain axis c = 9.4 Å compatible with regular conformation (A+TA+ trans A−TA− trans) of low energy having two constitutional repeating units although the diastereoselectivity is not regulated. In the WAXD pattern (Figure 5) of the oriented sample from the *t*-BuLi-MEE/MAD polymerization system (run 11), the diffraction peaks on layer lines could not be indexed with the fiber period c = 9.4 Å, but c = 7.0 Å was suggested by Polanyi's equation.[21] These results revealed that threo-disyndiotactic polymerization of MS occurred in the system. The fiber period of 7.0 Å suggested a possible conformation (S−G+S− trans S+G−S+ trans) for the threo(99%)-disyndiotactic(95%) poly(MS) as shown in Figure 6. The conformation was supported in the energy-minimization by a semiempirical molecular orbital method[11] using the oligomeric model, $CH_3{-}CH{=}CH{-}[CH(COOCH_3){-}C(CH_3){-}CH{=}CH]_n{-}CH_3$ (n = 10).

The streochemistries may account for the observed physical property difference. The erythro-diisotactic polymer has the T_g at 30 °C and melting endotherm (T_m) at 195 °C (ΔH = 31 J/g) (run 2 in Table 1), consistent with the previous report by Natta et al.[7b] A glass transition temperature (T_g) of poly(MS) with a threo/erythro ratio of 60/40 (run 1 in Table 1) was observed at 5 °C, whereas the T_g's of threo-disyndiotactic poly-

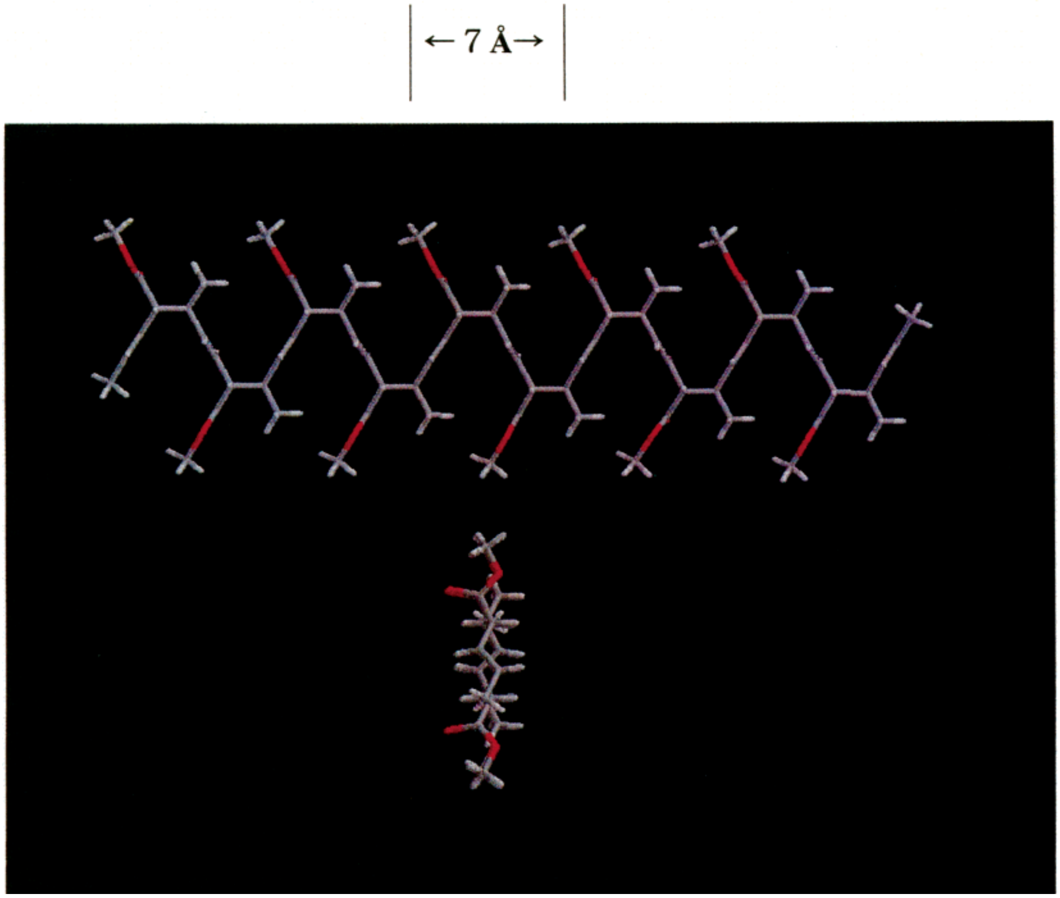


Figure 6. Side (top) and end (bottom) views of crystalline threo-disyndiotactic poly(MS) (n = 10) energy-minimized by PM3 method.

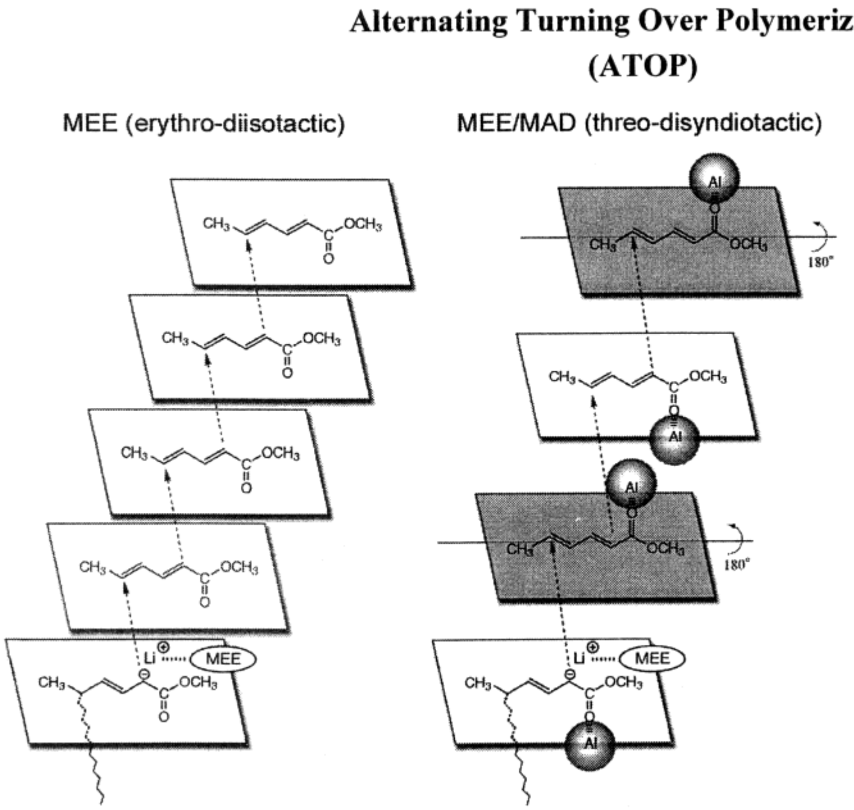


Figure 7. Stereospecific (threo-disyndiotactic) polymerization of alkyl sorbates via “alternating turning over polymerization (ATOP)” mechanism.

(MS)s were at 18−27 °C and increase with improvement of the stereochemistry. Threo(92%)-disyndiotactic(57%) poly(MS) showed the T_g at 18 °C, and threo(99%)-disyndiotactic(95%) poly(MS) showed the T_g at 27 °C accompanied by the T_m at 102 °C ($\Delta H = 22$ J/g). In the IR spectrum, some characteristic peaks (756 and 835 cm^{-1})[8a] due to the crystalline structure appeared. Interestingly, the difference (93 °C) of the T_m between erythro(100%)-diisotactic(81%) and threo(99%)-disyndiotactic(95%) poly(MS)s was much larger than the expected one. This is ascribed to the polymer chain-packing manner indicated by WAXS measurement.

The effect of the ester group on the stereochemistry was discussed using ethyl sorbate (ES). The polymerization results and the stereochemistry are summarized in Table 2. The polymerization conditions were same as those for MS except for the feed molar ratio of aluminum compound to the initiator ($[Al]_0/[I]_0$). In the case of $[Al]_0/[I]_0 = 3$, an anionic polymerization of ES did not occur at all (run 3), which is quite different from the results of MS. Coordination efficiency was apparently lower than that of MS. In the case of $[Al]_0/[I]_0 = 5$, the polymerization proceed to give threo-disyndiotactic poly(ES) quantitatively (run 4). The diastereoselectivity and tacticity could be evaluated by ^{13}C NMR measurements after hydrogenation. The threo diastereoselectivity was determined by signals due to $-CH_2-$ (25.5−26.2 ppm for erythro and 26.8−27.2 ppm for threo, $\Delta\delta = 1.15$ ppm) and carbonyl carbons (175.4 ppm for erythro and 175.0−175.1 ppm for threo, $\Delta\delta = 0.35$ ppm). The tacticity (diiso/disyndio) was calculated from the peak intensity ratio of two signals at 175.0 and 175.1 ppm. The stereochemistry was affected by temperature and additives, which is similar to that of poly(MS). Even at −20 °C, stereoregular poly(ES), i.e., threo(92%)-disyndiotactic(93%) poly(ES) could be synthesized. It seems that steric repulsion of alkyl group in ester groups improves both the diastereoselectivity (threo) and tacticity (disyndiotactic) in this polymerization mechanism.

Alternating Turning Over Polymerization (ATOP) Mechanism. In Figure 7, possible polymerization mechanisms in the *n*-BuLi-MEE/− and *t*-BuLi-MEE/MAD systems are shown. In the former, MS monomer seems to be inserted into the propagating anionic center from the same side to give erythro-diisotactic polymer, although Natta et al. did not discuss the polymerization mechanism at all.[7] As described previously, the MS dienolate in the polymer terminus prefer the s-trans conformation considerably relative to the s-cis conformation in the latter system (Figure 8). Therefore, the terminal unit seems to keep the “similar geometry” to *(E,E)*-alkyl sorbate. In fact, there are two addition types toward the propagating center. As the resulting polymer was threo-disyndiotactic, we could conclude that the polymerization proceed via trans addition (anti addition). From the results, we conclude that monomers were inserted with turning over alternatively toward the propagating center predominating s-trans conformation [“alternating turning over polymerization (ATOP)” mechanism] even in an isotropic state (Figure 7). This polymerization mechanism is essential for synthesis of the threo-disyndiotactic polymer.

This polymerization mechanism prompted us to consider a realistic strategy to synthesize erythro-disyndiotactic and threo-diisotactic polymers. Using *(Z,E)*-MS as the monomer, *t*-BuLi-MEE/MAD system should afford erythro-disyndiotactic poly(MS) via an “ATOP” mechanism, and the *n*-BuLi-MEE/− system would give threo-diisotactic poly(MS). The latter was expected to have a 3_1-helical conformation supported by a semiempirical molecular orbital calculation.[20] The polymerizations are now in progress. We will report more extensive work

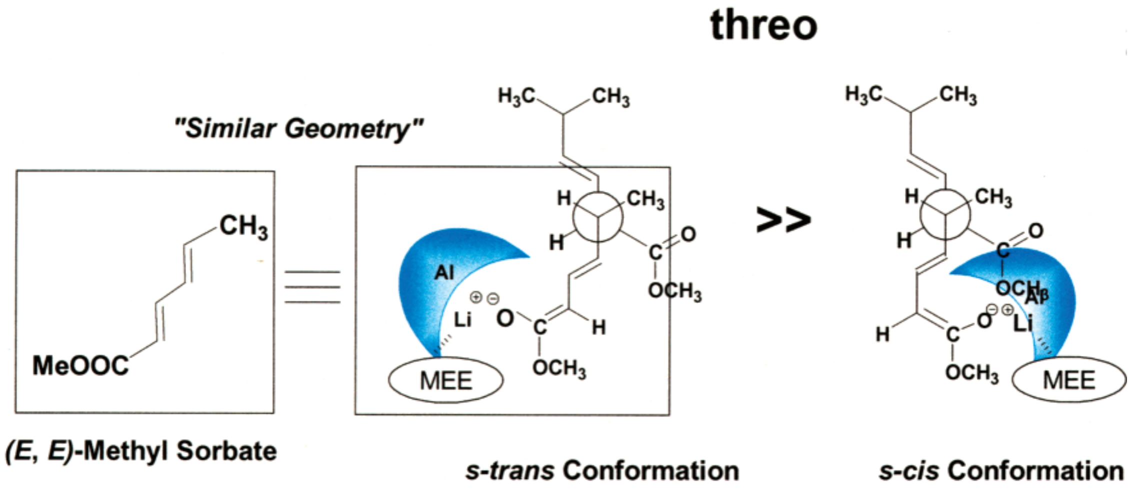


Figure 8. Newman projection formula of dimeric model compounds for the propagation end having s-trans (left) and s-cis conformations (right) of MAD-coordinated enolate.

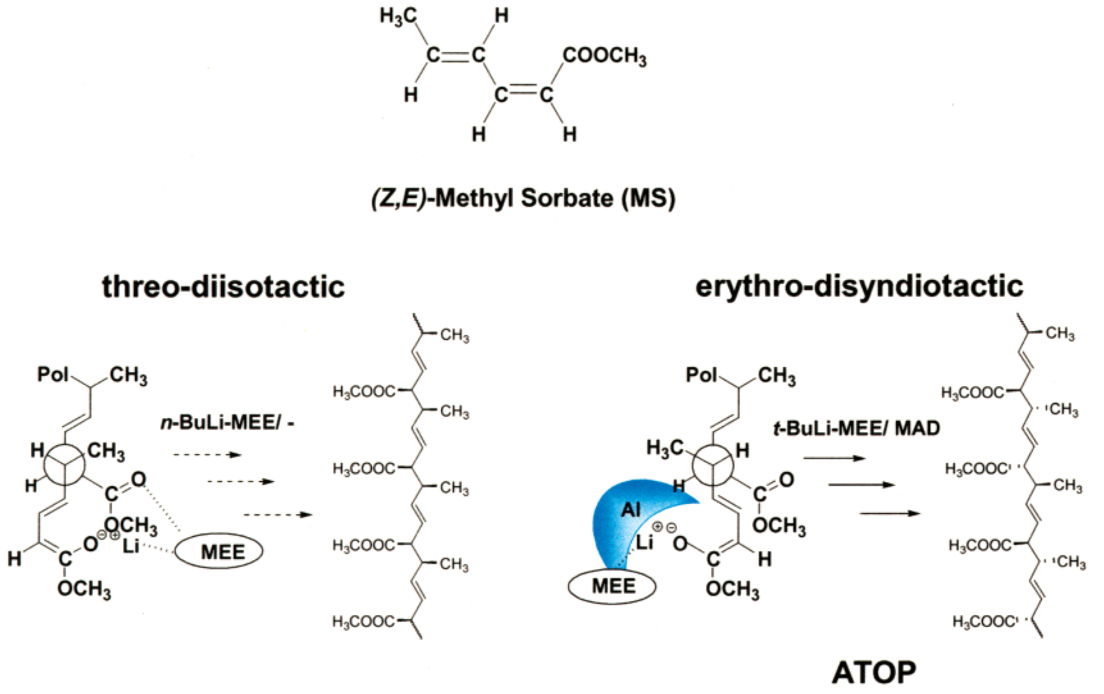


Figure 9. Synthetic strategy for threo-diisotactic and erythro-disyndiotactic poly(MS)s in anionic polymerization.

on stereospecific and asymmetric polymerizations of sorbic acid derivatives in the future.

Conclusions

We demonstrated bulky Lewis acid-catalyzed new type of stereospecific, threo(99%)-disyndiotactic(95%), anionic polymerization of a sorbic acid derivative by the "alternating turning over polymerization (ATOP)" mechanism. Polymerization in an isotropic state makes it possible to extend the number of monomer compared with solid-state polymerization. These fundamental data will be useful for designing stereoregular polymers and new materials using polar diene monomers.

Acknowledgment. Financial support to A.T. from the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Development Scientific Research, No. 13750816) is gratefully acknowledged. We are also grateful to Mr. Yutaka Yamauchi for his technical support of MEE synthesis.

References and Notes

(1) (a) Boor, J., Jr. *Ziegler Natta Catalyst and Polymerization*; Academic Press: New York, 1979. (b) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349. (c) Qin, M.; Bartus, J.; Vogl, O. *Macromol. Symp.* **1995**, *98*, 349.

(2) Brandrup, J., Immergut, E. H., Eds.; Polymer Handbook, 3rd ed.; Wiley: New York, 1989.

(3) Hirabayashi, T.; Yamamoto, H.; Kojima, T.; Takasu, A.; Inai, Y. *Macromolecules* **2000**, *33*, 4304.

(4) Takasu, A.; Yamamoto, H.; Inai, Y.; Hirabayashi, T.; Nagata, K.; Takahashi, K. *Macromolecules* **2001**, *34*, 6235.

(5) Takasu, A.; Ishi, M.; Inai, Y.; Hirabayashi, T. *Macromolecules* **2001**, *34*, 6548.

(6) Ordian, G. *Principles of Polymerization*, 3rd ed.; Wiley: New York, 1991; Chapter 8, pp 616−617.

(7) (a) Natta, G.; Farina, M.; Donati, M.; Peraldo, P.*Chim. Ind. Milan* **1960**, *42*, 1363. (b) Natta, G.; Farina, M.; Donati, M. *Makromol. Chem.* **1961**, *43*, 251. (c) Farina, M.; Corradini, P.; Gains, P. *J. Polym. Sci., Part A* **1965**, *2*, 11. (d) Farina, M.; Grassi, M.; Silvestro, G. Di; Zetta, L. *Eur. Polym. J.* **1985**, *21*, 71.

(8) (a) Fujio, R.; Sato, H.; Tsuruta, T. *Kogyo Kagaku Zasshi* **1966**, *69*, 2315. (b) Matsumoto, A.; Horie, A.; Otsu, T. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 681.

(9) Hertler, W. R.; RajanBabu, T. V.; Ovenall, D. W.; Reddy, G. S.; Sogah, D. Y. *J. Am. Chem. Soc.* **1988**, *110*, 5841.

(10) (a) Matsumoto, A.; Odani, T. *Polym. J.* **1998**, *31*, 717. (b) Matsumoto, A.; Nagahama, S.; Odani, T. *J. Am. Chem. Soc.* **2000**, *122*, 9109. (c) Matsumoto, A.; Sada, K.; Tashiro, K.; Miyata, M.; Tsubouchi, T.; Tanaka, T.; Odani, T.; Nagahama, S.; Tanaka, T.; Inoue, K.; Saragai, S.; Nakamoto, S. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 2502.

(11) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(12) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.

(13) Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Macromol. Chem. Suppl.* **1989**, *15*, 167.

(14) (a) Kitayama, T.; Zhang, Y.; Hatada, K. *Polym. J.* **1994**, *26*, 868. (b) Hirano, T.; Kitayama, T.; Hatada, K. *Polym. J.* **1998**, *30*, 736.

(15) Maruoka, K.; Itoh, T.; Sakura, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588.

(16) Saitou, S.; Ito, M.; Yamamoto, H. *J. Am. Chem. Soc.* **1997**, *119*, 611.

(17) Farina, M.; Silvestro, G. Di; Sozzani, P. *Macromolecules* **1982**, *15*, 1451.

(18) Mango, L. A.; Lenz, R. W. *Makromol. Chem.* **1973**, *163*, 13.

(19) BuLi-*tert*-diamine complexes initiated some anionic polymerizations in order to control stereoregularity or molecular weight. (a) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc.* **1979**, *101*, 4763. (b) Marchal, J.; Gnanou, Y.; Fontanille, M. *Macromol. Symp.* **1996**, *107*, 27. (c) Ochiai, B.; Tomita, I.; Endo, T. *Macromolecules* **1999**, *32*, 238.

(20) Corradini, P.; Napolitano, R.; Petraconne, V.; Pirozzi, B.; Tuzi, A. *Eur. Polym. J.* **1985**, *21*, 65.

(21) Tadokoro, H. *Structure of Crystalline Polymers*; John Wiley & Sons: New York, 1979.

MA030211Z