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Highly Threo Diastereoselective Anionic Polymerization of *(E,E)*-Methyl Sorbate Catalyzed by a Bulky Organoaluminum Lewis Acid

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Introduction. In contrast to recent progress in the control of the structure of vinyl polymers, that in the control of the structure of diene polymers including addition mode, geometry, and stereochemistry is not enough. Particularly, the stereochemistry is hard to regulate due to the inability to control the propagation step. However, physical properties of diolefin polymers such as polybutadiene and polyisoprene intensively depend on the polymeric stereoregularity.[1] Some stereoregular diolefin polymers have been synthesized with a transition metal catalyst.[2] We have investigated regioselective anionic polymerizations of 2-methyl-2,4-hexadienoate (MMHd)[3] and methyl 2,4-dimethyl-2,4-pentadienoate (MDMPd)[4] catalyzed by an organoaluminum compound. Furthermore, it was reported that subsequent hydrogenation of the polymers led to head-to-head (H−H) and head-to-tail (H−T) poly(propylene-*alt*-methyl methacrylate)s, respectively, as a first synthesis of well-defined poly(propylene-*alt*-methyl methacrylate).[4]

This paper describes threo diastereoselective polymerization of *(E,E)*-methyl sorbate (MS), that is, *(E,E)*-methyl 2,4-hexadienoate, by anionic polymerization in the presence of a bulky aluminum Lewis acid (Scheme 1). MS generates two adjacent chiral centers during the propagation step. It is of special importance to determine the diastereoselectivity of the process. Sorbic acid derivatives were polymerized by anionic,[5] radical,[6] group-transfer,[7] and topochemical (crystalline state)[8] polymerizations. Natta et al.[5] have described anionic polymerization of MS, which produced a highly stereoregular polymer with a 1,4-trans-*erythro*-diisotactic structure (tritactic polymer) by a chiral initiator[5a] or a chiral additive.[5a,b] Recently, Matsumoto et al. discovered that crystalline-state polymerization of the 1-naphthylmethylammonium salt of sorbic acid occurred stereospecifically to give the 1,4-trans-*erythro*-diisotactic polymer.[8] However, there are no reports for highly threo selective polymerization of sorbic acid derivatives as far as we know, although poly(MS) initiated by a butyllithium−tetramethylurea complex showed 75% threo diastereoselectivity.[5d] If there is any guide for the threo diastereoselective polymerization, it would be useful for control of the physical properties. We therefore undertook a far-reaching study aimed at synthesis of threo poly(sorbic acid derivative)s by Lewis acid coordinated polymerization in the isotropic state.

Results and Discussion. MS was polymerized in toluene at −20 °C using *tert*-butyllithium (*t*-BuLi) as the initiator in the presence of organoaluminum reagents (Table 1). The polymerization procedure was similar to that of MMHd or MDMPd.[3,4] All the resulting polymers were white solids and soluble in chloroform, tetrahydrofuran, and acetonitrile. Their structures were determined by IR and ^{1}H and ^{13}C NMR spectra.[9] ^{1}H NMR spectroscopy showed that resonance of the backbone methyl group was observed only at 0.96 ppm, characteristic of a methyl group on a saturated carbon rather than a vinylic carbon. This excluded the possibility of any 1,2- or 3,4-additions. ^{13}C NMR also supported complete 1,4-addition. IR absorption of the residual double bond in the main chain was observed at 971 (δ_{C-H}) cm^{-1}, indicating trans geometry. 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,[10] the proton-decoupled resonance signals of carbons were all single and differed by 1.4 ppm in the ^{13}C NMR spectrum. Hertler et al.[7] reported that Michael addition-type group-transfer polymerization of MS gave polymer composed of cis (22%) and trans (78%) structure, in which methine carbons of *C*HCH$_3$ (40.34 and 40.54 ppm) and *C*HCOOCH$_3$ (55.71 and 56.46 ppm) in the trans structure were distinguishable from those in the cis structure [*C*HCH$_3$ (35.48 ppm), *C*HCOOCH$_3$ (50.43 and 50.97 ppm)]. Poly(MS)s obtained in this study exhibited resonances at 38.7−39.8 (*C*HCH$_3$) and 54.8−55.4 (*C*HCOOCH$_3$), and the peaks assigned to the cis structure were not observed at all.

In the absence of an organoaluminum compound, control of molecular weight and molecular weight distribution was difficult (run 1). The molecular weight of the poly(MS) ($M_n = 6.2 \times 10^4$) determined by size

Scheme 1. Threo Diastereoselective Polymerization of MS and Subsequent Hydrogenation

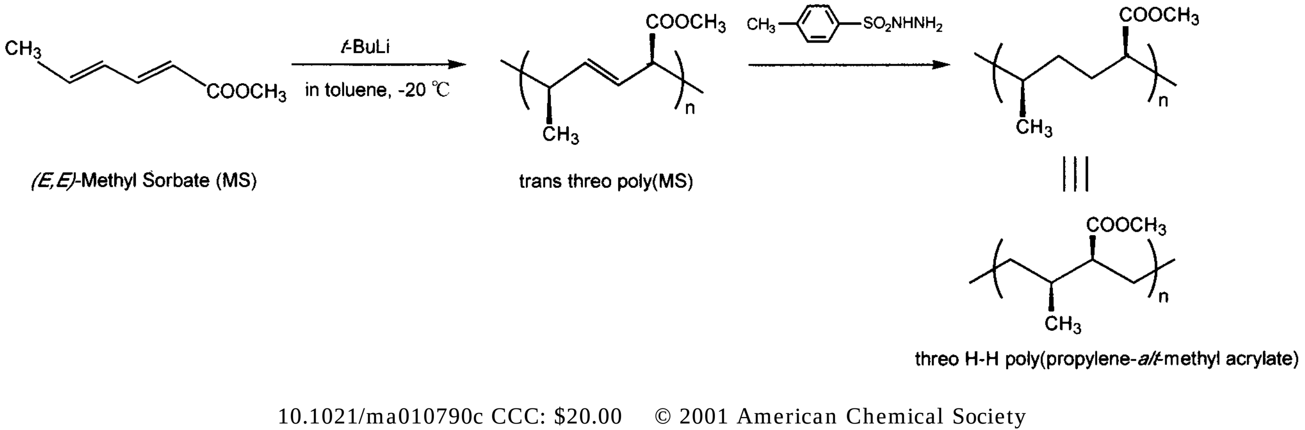

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Table 1. Anionic Polymerization of Methyl Sorbate (MS) in Toluene at − 20 °C,^{a} and the Diastereoselectivity

									hydrogenation^{f}	
run	initiator	additive^{b}	time (h)	yield (%)	$10^{-4}M_n$^{c}	M_w/M_n^{c}	I_{eff}^{d} (%)	T_g^{e} (°C)	yield (%)	erythro/threo^{g}
1	*t*-BuLi		72	28	6.2	2.8_7	3	5	96	60/40
2	*t*-BuLi	*i*-Bu$_3$Al	72	0						
3	*t*-BuLi	MAD^{h}	72	96	4.5	1.6_2	14	20	98	8/92
4	*t*-BuLi	MAD^{h}	168	98	5.4	1.4_6	12	21	84	8/92
5	*t*-BuLi	ATPH^{i}	72	0						
6	*t*-BuLi	EADP^{i}	72	0						
7	*t*-BuLi−Sp^{k}		200	3	2.3	1.4_6	1			
8	*t*-BuLi−Sp^{k}	MAD^{h}	72	79	3.1	1.23	16	18	84	6/94

[a] $[M]_0$ = 1.5 mol/L. $[M]_0/[I]_0$ = 50. [b] Feed molar ratio of aluminum compound to initiator ($[Al]_0/[I]_0$) = 3. [c] Determined by SEC in THF relative to polystyrene. [d] Initiator efficiency, defined as [(MW of monomer) × $[M]_0/[I]_0$ × yield/100]/M_n. [e] Determined by DSC (heating rate: 10 °C /min). [f] [repeating unit]$_0$ = 0.16 mol/L in toluene at 110 °C for 168 h; $[TSH]_0$/[repeating unit]$_0$ = 3.0. [g] Determined by ^{13}C NMR measurement in CDCl$_3$ after hydrogenation. [h] Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide). [i] Aluminum tris(2,6-diphenylphenoxide). [j] Ethylaluminum bis(2,6-diphenylphenoxide). [k] (−)-Sparteine.

exclusion chromatography (SEC) was higher than that calculated from the monomer/initiator ratio [M_n(calcd) = 0.63 × 10^4], and the molecular weight distribution was broad ($M_w/M_n = 2.8_7$). The broad molecular weight distributions might be due to attack of the polymer anion at the carbonyl group of the MS monomer. Hatada et al. have reported that polymerization of methyl methacrylate by a *t*-BuLi/organoaluminum compound produces stereoregular poly(methyl methacrylate) with narrow molecular weight distributions in toluene.[11,12] We used similar initiator systems to that used for the polymerization. For MS, it is considered that coordination of a Lewis acid to the carbonyl group promotes the 1,4-addition and simultaneously prevents the carbonyl attack on the ester group. The coordination of various bulky aluminum compounds was confirmed by ^{13}C NMR measurement in toluene-d_6. δ-Carbon (138.8 ppm) of the MS monomer shifted toward lower field in the 1:1 mixtures (mole/mole) of MS/aluminum compound, MS/triisobutylaluminum (*i*-Bu$_3$Al) (142.6 ppm), MS/methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenoxide) (MAD)[13] (145.1 ppm), MS/aluminum tris(2,6-diphenylphenoxide) (ATPH)[14] (141.2 ppm), and ethylaluminum bis(2,6-diphenylphenoxide) (EADP) (141.5 ppm). Unexpectedly, MS was scarcely polymerized except for *t*-BuLi/MAD initiator systems. It is known that organoaluminum aryloxides are bulky but do not reduce the Lewis acidity much.[13] MAD was suitable for the polymerization to produce polymers with relatively narrow molecular weight distributions in excellent yield (runs 3 and 4), although the initiator efficiency (I_{eff}) was still low. It seemed that more bulky organoaluminum compounds, both ATPH and EADP, suppressed the polymerization (runs 5 and 6). In the high-resolution (100 MHz) ^{13}C NMR spectrum of the polymer, splitting of the resonance assigned to COOCH_3 is observed at 51.4 and 51.6 ppm, which is considered to be ascribed to the erythro/threo configuration[5d] because the geometry in the double bond is confirmed to be all trans. In the spectrum of poly(MS) prepared by *t*-BuLi/MAD, only a sharp signal at 51.6 ppm was observed.[9] We found that anionic polymerization of MS in the presence of MAD occurred threo diastereoselectively. However, this ^{13}C NMR analysis did not allow us to quantify the ratio of erythro/threo structures because of overlapping of the peaks; that is, their chemical shift difference ($\Delta\nu$) was very low (0.02 ppm).

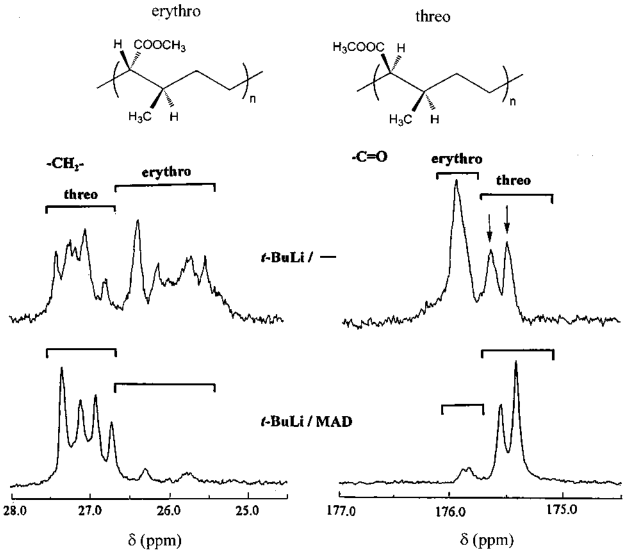

Figure 1. Expanded ^{13}C NMR spectra (in CDCl$_3$) of hydrogenated poly(MS)s, prepared by *t*-BuLi/− (top) and *t*-BuLi/MAD (bottom) initiator systems.

Hydrogenation of the internal double bonds made it possible to evaluate the stereochemistry in detail. This technique has already been found to be effective in the study of the tacticities of 1,4-polydienes.[5d,15] The poly(MS)s were converted to the saturated polymer, that is, H−H poly(propylene-*alt*-methyl acrylate), by diimide generated by thermal decomposition of *p*-toluenesulfonylhydrazide (TSH)[4,16] (yield, 84−98%).[17] The molecular weights of the hydrogenated polymer [M_n and M_w/M_n of poly(MS) from run 4 were 5.4 × 10^4 and 1.4_6] indicated that hydrogenation proceeded without main chain scission (those of hydrogenated polymer were 5.8 × 10^4 and 1.4_8). The ^{13}C NMR spectrum of the hydrogenated poly(MS) prepared by *t*-BuLi/MAD is shown in Figure 1, together with that of hydrogenated poly(MS) from *t*-BuLi initiator. The clear peaks for the main chain (COCHCH$_2$) and carbonyl carbons were depicted for the former, being different from the broad and multiple resonances for the latter spectrum. The chemical shifts came to reflect their different stereochemistries clearly ($\Delta\nu$ 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, $\Delta\nu$ = 1.35 ppm) and the carbonyl carbons (175.8−176.2 ppm for erythro and 175.2−175.7 ppm for threo, $\Delta\nu$ = 0.55 ppm). The erythro and threo ^{13}C NMR assignments were identified with those of poly(MS)s made by anionic[5d] and group-transfer[7] polymerizations and were confirmed by a model compound, 5-methoxycarbonyl-2,6,9-trimethyldecane.[5d]

The erythro/threo ratio of hydrogenated poly(MS) from the *t*-BuLi/MAD system was determined to be 8/92, while that for poly(MS) from the *t*-BuLi/− system was 60/40. This is the first example of highly threo diastereoselective polymerization of a sorbic acid derivative as far as we know. These factors may account for the observed physical property difference. The glass transition temperature of poly(MS) with an erythro/threo ratio of 40/60 was observed at 5 °C , whereas the threo poly(MS)s showed the transition at 20−21 °C . If we consider the erythro and threo structures generated by a propagating step (antiperiplanar transition state), there is a greater number of nonbonded interactions[7] in the threo adduct than in the erythro adduct in the absence of MAD. When a polymer anion is coordinated with MAD, there might be fewer unfavorable nonbonded interactions in the threo adduct. There are two types of possible stereoregular structures for the trans-*threo*-1,4-polymer (diisodiotactic and disyndiotactic).[18] Interestingly, the resonance of the threo carbonyl carbon was clearly split into two peaks (arrow marks in Figure 1), which were considered to be ascribed to the two steroisomers. However, we have not assigned their peaks yet. The intensity ratio of the peaks ($I_{175.3\ \mathrm{ppm}}/I_{175.6\ \mathrm{ppm}}$) increased from 51/49 (*t*-BuLi/−) to 57/43 (*t*-BuLi/MAD). These results show that coordination of MAD improves the tacticity as well as the threo diastereoselectivity.

MAD/(−)-sparteine (Sp)[19] initiator (run 8) was effective for improvement of the molecular weight distribution ($M_w/M_n = 1.2_3$) as well as the threo diastereoselectivity (erythro/threo = 6/94). Although the difference of the diastereoselectivity is little compared with that of the *t*-BuLi/MAD system, apparent changes of the spectrum pattern were confirmed. In the ^{13}C NMR spectrum, the intensity ratio $I_{175.3\ \mathrm{ppm}}/I_{175.6\ \mathrm{ppm}}$ increased from 60/40 to 70/30, indicating improved tacticity. In the IR spectrum, some characteristic peaks (756 and 835 cm^{-1})[6a] due to crystalline structure appeared. Among threo poly(MS)s, *threo*-diisotactic polymers possess optical activity, while *threo*-disyndiotactic polymers do not because of the existence of a mirror glide plane.[18] *t*-BuLi−Sp initiator has a possibility to produce asymmetric polymers having a preferred screw sense. In circular dichroism measurements of the polymer, we could not find any clear Cotton effect (200−600 nm). This might be due to the irregularity of diiso/disyndiotacticity. We will report more extensive work on threo diastereoselective, stereospecific, asymmetric polymerizations of sorbic acid derivatives and the mechanism in the future.

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(9) For poly(MS) (96% yield, run 3 in Table 1). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.96 (CHC*H*$_3$), 2.58 (C*H*CH$_3$), 2.81 (C*H*CO), 3.65 (OC*H*$_3$), 5.32−5.38 (═C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 17.6−18.7 (CH*C*H$_3$), 38.7−39.8 (*C*HCH$_3$), 51.6 (O*C*H$_3$), 55.0 (*C*HCO), 125.6−127.0 (═*C*HCHCH$_3$), 135.7−136.5 (═*C*HCHCO), 173.6 (*C*OOCH$_3$). IR (KBr disk, cm^{-1}): 2843 (ν_{CH}), 1735 [$\nu_{\mathrm{C=O}}$(ester)], 1667 ($\nu_{\mathrm{C=C}}$), 1435 (δ_{CH}), 1254 and 1161 [ν_{COC}(ester)], 971 ($\delta_{\mathrm{C=CH}}$).

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(17) The experimental procedure was the same as that for hydrogenation of poly(MMHd) or poly(MDMPd) in our previous report.[4] For poly(propylene-*alt*-MA) (98% yield, run 3 in Table 1). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 0.81, 0.98 (CHC*H*$_3$), 1.25 (C*H*$_2$CHCH$_3$), 1.39 (C*H*$_2$CHCO), 1.57 (C*H*CH$_3$), 2.14 (C*H*CO), 3.59 (OC*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 16.4−16.9 (CH*C*H$_3$), 25.8, 26.3 (erythro), 26.6, 27.8, 27.1, 27.3 (threo) (*C*H$_2$CHCO), 32.3, 32.4, 32.9 (*C*H$_2$CHCH$_3$), 35.3, 35.5, 35.8, 35.9 (*C*HCH$_3$), 50.6−50.9 (COO*C*H$_3$), 51.1 (threo) (*C*HCO), 175.3, 175.6 (threo), 175.8, 175.9 (erythro) (*C*OOCH$_3$). IR (KBr disk, cm^{-1}): 2924 (ν_{CH}), 1734 [$\nu_{\mathrm{C=O}}$(ester)], 1457 (δ_{CH}), 1166 [ν_{COC}(ester)].

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